

Two solvatomorphic forms of a copper complex formulated as $\text{Cu}(L^1)(\text{ClO}_4)_2 \cdot 1.2\text{H}_2\text{O}$ and $\text{Cu}(L^1)(\text{ClO}_4)_2$, where L^1 is 3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane

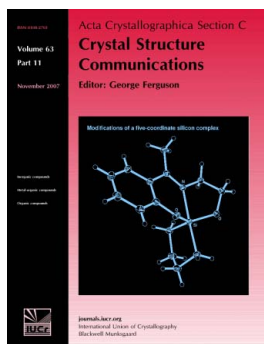
Babul Chandra Nath, Sebastián Suarez, Fabio Doctorovich, Tapashi G. Roy and Ricardo Baggio

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Two solvatomorphic forms of a copper complex formulated as $\text{Cu}(L^1)(\text{ClO}_4)_2 \cdot 1.2\text{H}_2\text{O}$ and $\text{Cu}(L^1)(\text{ClO}_4)_2$, where L^1 is 3,10-*C-meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane

Babul Chandra Nath,^a Sebastián Suarez,^{b*} Fabio Doctorovich,^b Tapashi G. Roy^a and Ricardo Baggio^c

^aUniversity of Chittagong, Chittagong 4331, Bangladesh, ^bDepartamento de Química Inorgánica, Analítica y Química Física/INQUIMAE-CONICET, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina, and ^cGerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
Correspondence e-mail: seba@qi.fcen.uba.ar

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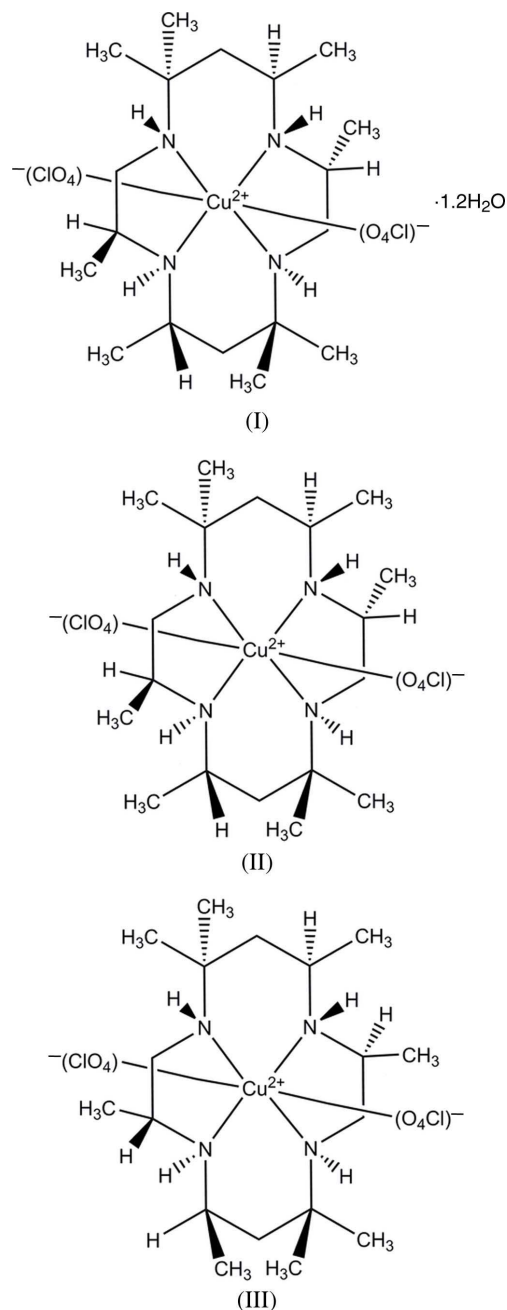
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Two copper complex solvatomorphs, namely (3,10-*C-meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane)bis(perchlorato- κO)copper(II) 1.2-hydrate, $[\text{Cu}(\text{ClO}_4)_2(\text{C}_{18}\text{H}_{40}\text{N}_4)] \cdot 1.2\text{H}_2\text{O}$, (I), and (3,10-*C-meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane)bis(perchlorato- κO)copper(II), $[\text{Cu}(\text{ClO}_4)_2(\text{C}_{18}\text{H}_{40}\text{N}_4)]$, (II), are described and compared with each other and with a third, already reported, anhydrous diastereomer, denoted (III). Both compounds present very similar centrosymmetric coordination environments, with the Cu^{II} cation lying on an inversion centre in a distorted 4+2 octahedral environment, defined by the macrocyclic N_4 group in the equatorial sites and two perchlorate groups in *trans*-axial positions [one of the perchlorate ligands in (I) is partially disordered]. The most significant difference in molecular shape is seen in the orientation of the perchlorate anions, and the influence of this on the intramolecular hydrogen bonding is discussed. The (partially) hydrated state of (I) favours the formation of chains along [011], while the anhydrous character of (II) and (III) promotes loosely bound structures with low packing indices.

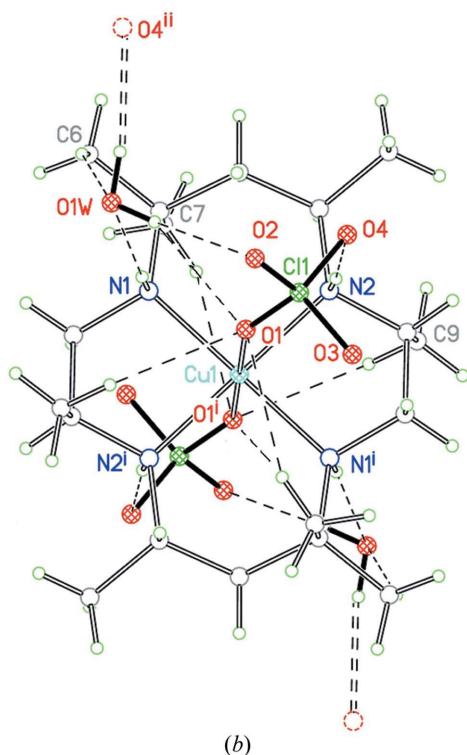
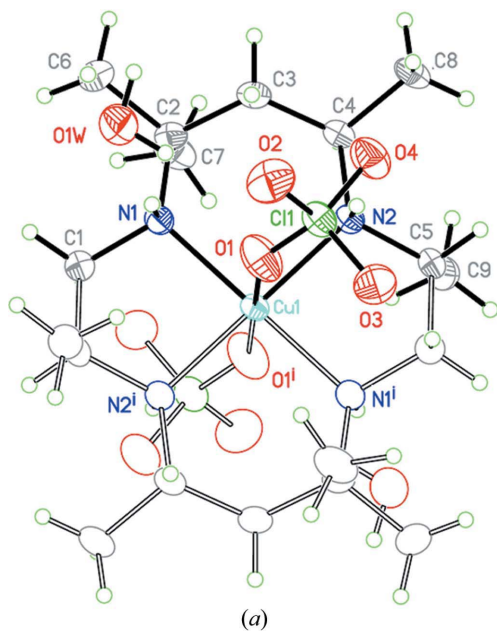
Comment

Synthetic macrocyclic complexes are important in view of their presence in many biologically significant and naturally occurring metal complexes, such as vitamin B12, haemoglobin and chlorophyll, all of which play vital roles in biological systems (Bernhardt & Lawrance, 1990; Reid & Schroder, 1990). Saturated tetraaza macrocycles have proven to be

versatile macrocyclic ligands capable of forming stable inert complexes with a variety of biomedically important metal ions, the chemistry of which has attracted interest due to their involvement in a variety of catalytic, biochemical and industrial processes (Kimura *et al.*, 1992, 1994). Regarding biological applications, metal complexes of the 14-membered tetraaza macrocyclic ligands directly relevant to the present

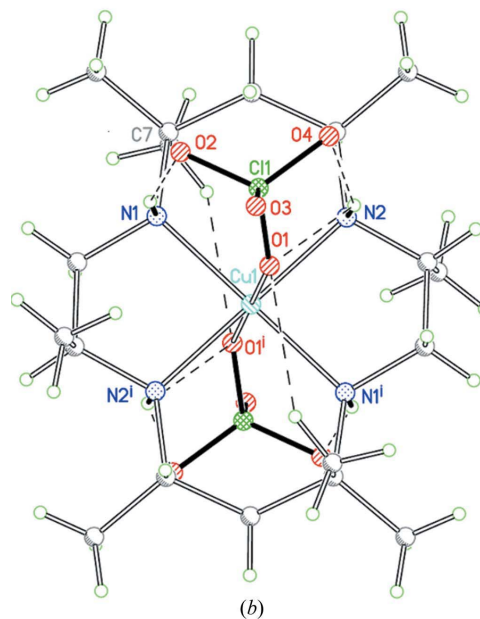
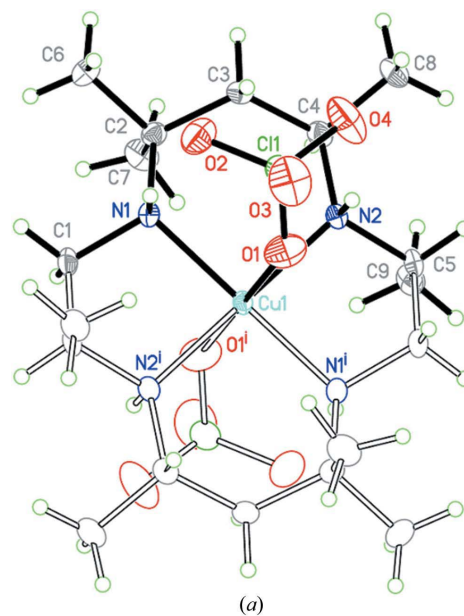


study have been explored for their use in magnetic resonance imaging (MRI) and radioimmunotherapy (Norman *et al.*, 1995; König *et al.*, 1996). They are also useful in terms of their utility in pharmacological (Hollinshead & Smith, 1990), crystal engineering (Suh *et al.*, 2006) and analytical (Singh *et al.*, 1999) endeavours, and they have been found to have antifungal (Roy, Hazari, Dey, Meah *et al.*, 2007), antibacterial (Roy, Hazari, Dey, Miah *et al.*, 2007; Roy, Hazari, Dey, Nath *et al.*,


Figure 1

(a) Displacement ellipsoid plot of (I), drawn at the 40% probability level. (b) The hydrogen-bonding scheme for (I) (dashed lines). In both, only the major part of the disordered perchlorate anion is drawn. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z$.]

2007) and (in some cases) potential anticancer properties (Arai *et al.*, 1998; Gao *et al.*, 2010). All the aforementioned potential applications have promoted strong sustained research on the subject and, in this respect, we refer the interested reader to a recent review accounting for a 50 year period of research on this type of compound (Curtis, 2012), where a large number of differently *N*-substituted (*viz.* methyl, propyl and allyl) macrocyclic ligands complexed to a


Figure 2

(a) Displacement ellipsoid plot of (II), drawn at the 40% probability level. (b) The hydrogen-bonding scheme for (II) (dashed lines). [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

variety of cations (*e.g.* Cu, Co, Cr, Zn, Cd and Pd) are analysed.

As a continuation of a current area of research in our laboratory (Hazari *et al.*, 1999; Roy & Bembí, 2005; Roy *et al.*, 2006), we present herein the crystal structures of the title solvatomorphic variants $\text{Cu}(\text{ClO}_4)_2(L^1) \cdot 1.2\text{H}_2\text{O}$, (I), and $\text{Cu}(\text{ClO}_4)_2(L^1)$, (II), two mixed Cu^{II} complexes having perchlorate as the inorganic balancing anion and L^1 , an isomeric form of L (= 3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane), as the organic ligand.

Even though a large number of analogous $\text{Cu}^{\text{II}}-L$ complexes have been reported with perchlorate as the counter-anion, *viz.* those presented by Lee *et al.* (1985) and Hazari *et*

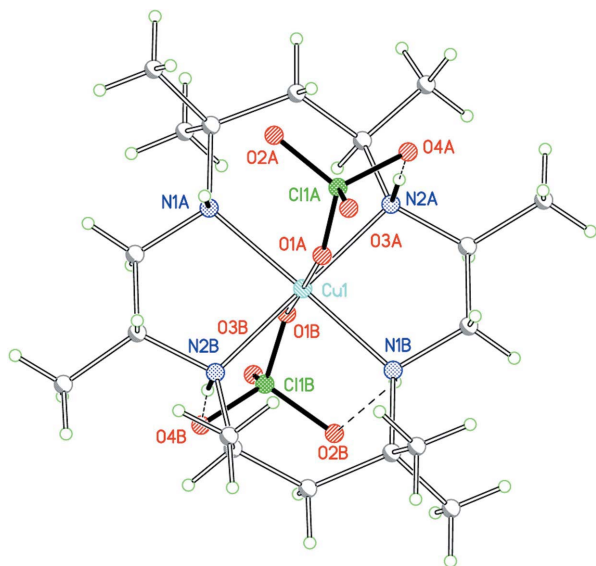


Figure 3
Ball-and-stick plot of (III) (Lin *et al.*, 2006), showing the intramolecular hydrogen-bonding scheme (dashed lines).

al. (2001), only one has the anion behaving in the coordinating mode observed in (I) and (II), *i.e.* the anhydrate diastereomer reported by Lin *et al.* (2006), hereinafter (III), with which we shall compare our results.

Displacement ellipsoid views of (I) and (II) are shown in Figs. 1(a) and 2(a), respectively, while (III) is shown in Fig. 3. The very similar centrosymmetric coordination environments in (I) and (II) (a distorted 4+2 octahedron) present the macrocycle N_4 group occupying the equatorial (eq) sites and two perchlorate groups in *trans*-axial (ax) positions, one perchlorate group in (I) being partially disordered (see *Refinement* section for details). Coordination distances can be found in Tables 1 and 3. The 14-membered rings have the usual zigzag shape and present four equatorial and four axial methyl groups, the latter groups in pairs, *trans* to each other due to centrosymmetry. Independent amine atoms N1 and N2 present their H atoms on the same side of the coordination plane and opposite the neighbouring axial methyl groups (Figs. 1a and 2a). The similarity of both central cores can be envisaged from Fig. 4, which presents a least-squares fit of just the basal coordination planes. It is clearly seen that only the orientations of the pendant perchlorate anions differ substantially. We shall see below the influence this has on the intramolecular hydrogen bonding.

Due to coordination, the 14-membered ligand generates four smaller rings, two six-membered rings in chair conformations and two five-membered rings in half-chair forms.

The Cu– N_{eq} bond lengths are similar in (I) and (II) (see Tables 1 and 3), while the corresponding bond angles differ from the ideal value of 90° by ± 4.25 (12) and 4.66 (7) $^\circ$ for (I) and (II), respectively. As expected, the Cu– O_{ax} bond lengths for both compounds (*ca.* 2.83 Å) are significantly longer than the Cu– N_{eq} ones, and are also longer than the typical axial values for CuN_4O_2 complexes [mean value = 2.47 (16) Å for 1622 entries in the Cambridge Structural Database (CSD,

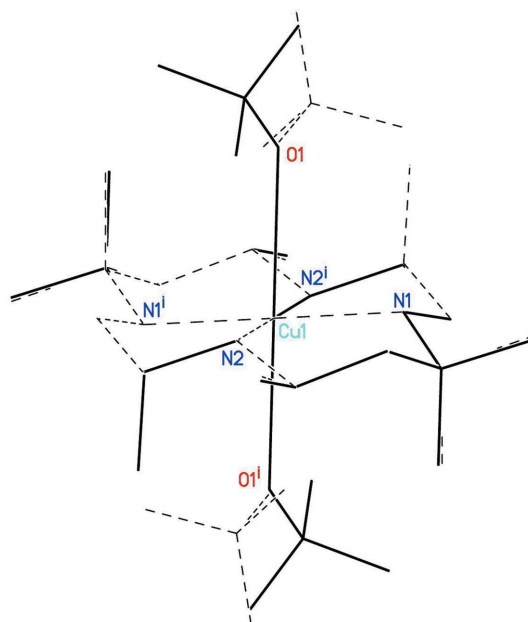


Figure 4

Schematic superposition of (I) (full lines) and (II) (broken lines), where only the CuN_4 cores were included in a least-squares match. Note the almost perfect fit displayed by the *L* ligands and the (rotational) misfit in the pendant perchlorate anions. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

Version 5.3; Allen, 2002)]. The axial coordination is rather tilted, *viz.* subtending angles with the basal mean plane of 15.32 (2) and 13.74 (3) $^\circ$ for (I) and (II), respectively. The structures appear more regular than in the diastereomer (III), which shows wider bond and angle ranges [Cu–N = 2.015 (2)–2.048 (2) Å and C–O = 2.570 (3)–2.731 (3) Å; basal angles = 90 ± 5.73 (7) $^\circ$], but presents more ‘vertical’ apical bonds [angles to the basal mean plane = 9.30 (4) and 5.72 (5) $^\circ$].

In a centrosymmetric *L* ligand, there are four independent chiral centres (N1, C4, N2 and C5) and, accordingly, $2^4 = 16$ possible configurations to be expected. The sequence observed for L^1 in both (I) and (II) is *RRRR*–*SSSS*. In compound (III), the complex we chose for comparison, the isomeric L^2 variant is not centrosymmetric and presents an *RRRS*–*SRSR* distribution of the same sequence of chiral centres. There are two main differences to be noted: (i) a different set-up in what would be the ‘independent part’ [*RRRR* in (I) and (II) and *RRRS* in (III), *viz.* different chirality at atom C5]; (ii) a noncentrosymmetric relationship at sites C4–C4A [*R*–*S* in (I) and (II), and *R*–*R* in (III)]. Fig. 5 presents a schematic view of all three configurations, with the critical zones encircled, highlighting the differences between the (I)–(II) pair and (III).

A search of the CSD disclosed, in addition to (I) and (II), 14 other transition metal complexes with different diastereomers of the *L* ligand and the same chiral centres (see Table 5 for some relevant information). Only two of these 16 structures crystallize in a noncentrosymmetric space group. Of the 14 centrosymmetric structures, seven present the central cation lying on a centre of symmetry. An analysis of the distribution

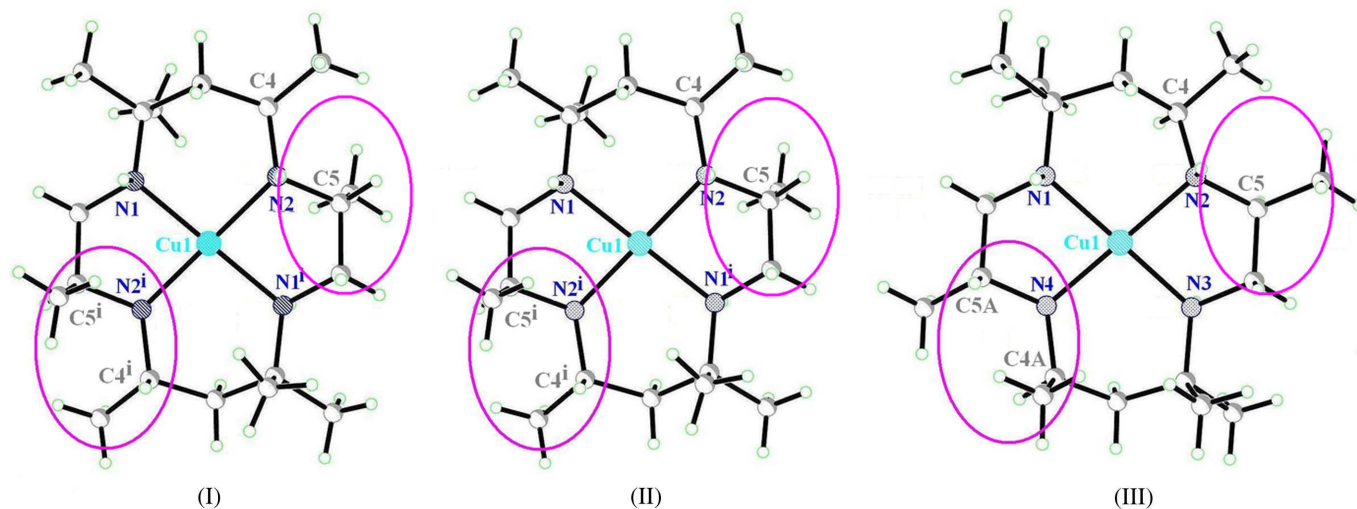


Figure 5
Schematic representation of the configurations in (I), (II) and (III). Encircled are the critical zones highlighting the differences between the (I)–(II) pair and (III). [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

of chiral centres suggests the overall distribution to be far from random; there are a total of eight different arrays with quite uneven population structures presenting the *RRRR*–*SSSS* distribution reported here, referred to as type 1 in Table 5, and these correspond to centrosymmetric molecules. Half of the remaining cases are bunched into a three-membered group (type 2) and a two-membered group (type 3), while the remaining five distributions are unique and present no duplication.

These different configurations lead to different orientations between hydrogen-bonding donors and acceptors, either facilitating or hampering some intramolecular interactions. Those in (I) and (II) are presented in Tables 2 (entries 1–7) and 4 (entries 1–4), respectively, and shown in Figs. 1(b) and 2(b). For completeness, the interactions in (III) are shown in Fig. 3. The most notable difference is that (II) has both amino H atoms involved in hydrogen bonds with perchlorate O atoms as acceptors. In the case of (I), instead, the $R(6)$ (N1–H1...O2–Cl1–O1–Cu1) ring present in (II) (Bernstein *et al.*, 1995) opens, making room for the (depleted) O1W water

molecule, which thus gives rise to an enlarged $R_2^2(8)$ (N1–H1...O1W–H1WA...O2–Cl1–O1–Cu1) loop. In addition, a small $R_1^2(4)$ (H1WA...O1–Cl1–O2...O1) ring is built up. The presence of this (depleted) water molecule strongly anchored to the complex molecule gives rise to the second difference concerning intermolecular interactions, *viz.* the remaining atom H1WB, which is not involved in intramolecular contacts, forms a hydrogen bond to a neighbouring perchlorate ligand (eighth entry in Table 2), defining a pair of centrosymmetric hydrogen-bonded $R_4^2(12)$ rings and generating a one-dimensional structure parallel to [011], shown in Fig. 6 together with the rings generated.

A hasty hydrogen-bonding analysis might erroneously lead to the conclusion that the minor-occupancy perchlorate atom

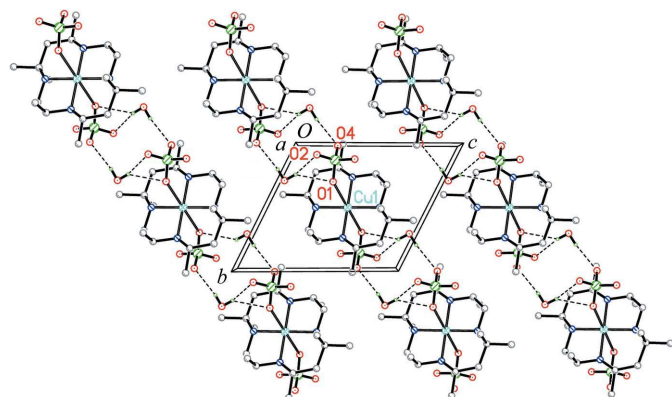


Figure 6
A packing view of (I), showing the one-dimensional chains running in the [011] direction. Dashed lines indicate hydrogen bonds.

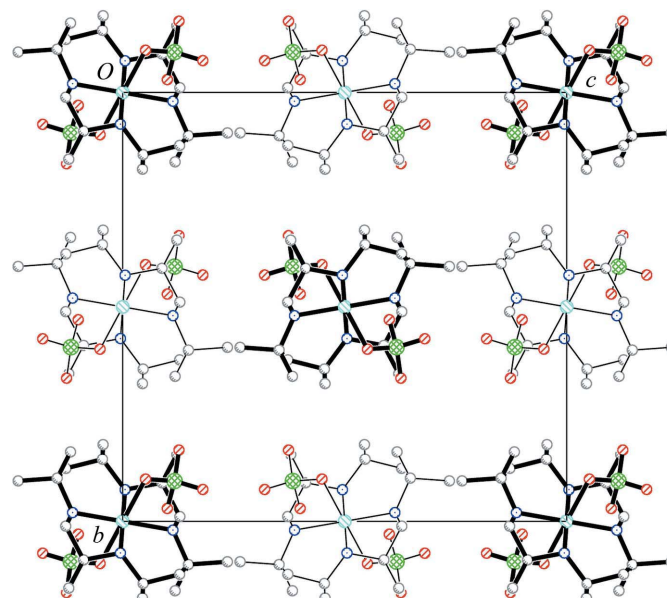


Figure 7
A packing view of (II), with molecules drawn with thin lines lying at $x = 0$ and those drawn with heavy lines lying at $x = \frac{1}{2}$.

Table 1
Selected bond lengths (Å) for (I).

Cu1—N1	2.020 (3)	Cu1—O1	2.833 (4)
Cu1—N2	2.023 (3)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...O1W	0.91	2.38	3.261 (9)	163
N2—H2N...O4	0.91	2.23	3.138 (6)	173
C7—H7C...O1 ⁱ	0.96	2.52	3.437 (7)	159
C9—H9A...O1 ⁱ	0.96	2.47	3.412 (7)	168
O1W—H1WA...O2	0.85 (1)	2.44 (9)	3.137 (9)	139 (12)
O1W—H1WA...O1	0.85 (1)	2.22 (4)	3.029 (9)	159 (11)
O1W—H1WB...O4 ⁱⁱ	0.85 (1)	2.17 (6)	2.967 (8)	155 (12)

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

O3' 'bumps into' water atom H1WA [H1WA...O3' = 1.003 (3) Å]. However, this is only an artifact derived from the fact that both units (the water solvent and the minor part of the perchlorate anion) have incomplete occupancies, allowing for one of the groups to be present while the other is not, and *vice versa*, so that the apparent interaction is in fact only illusory.

In contrast with (I), the structure of (II) does not show any relevant intermolecular interactions, and the crystal structure can be described as the packing of 'spheres', held together by very weak forces of the van der Waals type. Fig. 7 shows a packing view where this set-up is apparent.

Structure (III) shares its anhydrous character with (II), and with this the lack of significant intermolecular interactions. This shows up in the rather low packing indices [66.1% for (II) and 66.2% for (III), calculated using *PLATON* (Spek, 2009)]. For comparison, the same index for (I) is 69.8% (only the major part of the disordered anion has been considered in the calculation).

Experimental

For the synthesis of *L*, reduction of 3,10-*C-meso*-Me₈[14]diene dihydroperchlorate (Curtis *et al.*, 1969) and resolution of isomeric Me₈[14]anes were carried out as described in the literature (Bembi *et al.*, 1989); ligand *L* in the present work corresponds to *Lb* in the latter cited paper. Regarding chirality, in the diene ligand there were originally two chiral centres and the reduction process gives rise to two further chiral centres.

For the synthesis of the copper(II) diperchlorate complexes (I) and (II), copper(II) perchlorate hexahydrate (0.371 g, 1.0 mmol) and *L* dihydrate (0.320 g, 1.0 mmol) were dissolved separately in hot methanol (50 ml). The colourless ligand solution was added as soon as possible to the copper salt solution while hot. An intense blue solution appeared within a few minutes. The resulting mixture was allowed to evaporate slowly and dark-blue crystals appeared. These were filtered off and recrystallized from a minimum quantity of aqueous methanol (1:1 *v/v*). Crystals of both (I) and (II), differentiated by their shape, appeared in the same recrystallization process.

Table 3
Selected bond lengths (Å) for (II).

Cu1—N1	2.0270 (19)	Cu1—O1	2.831 (3)
Cu1—N2	2.0295 (19)		

Compound (I)

Crystal data

[Cu(ClO ₄) ₂ (C ₁₈ H ₄₀ N ₄)]·1.2H ₂ O	$\gamma = 98.616 (11)^\circ$
$M_r = 596.61$	$V = 672.67 (17) \text{ \AA}^3$
Triclinic, <i>P</i> $\bar{1}$	$Z = 1$
$a = 8.5783 (10) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.7819 (12) \text{ \AA}$	$\mu = 1.06 \text{ mm}^{-1}$
$c = 10.2156 (13) \text{ \AA}$	$T = 294 \text{ K}$
$\alpha = 114.835 (13)^\circ$	$0.35 \times 0.25 \times 0.20 \text{ mm}$
$\beta = 98.036 (10)^\circ$	

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer	9475 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	3193 independent reflections
$T_{\min} = 0.72, T_{\max} = 0.82$	2285 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.057$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.170$	
$S = 0.93$	$\Delta\rho_{\max} = 0.73 \text{ e \AA}^{-3}$
3193 reflections	$\Delta\rho_{\min} = -0.49 \text{ e \AA}^{-3}$
183 parameters	
97 restraints	

Compound (II)

Crystal data

[Cu(ClO ₄) ₂ (C ₁₈ H ₄₀ N ₄)]	$V = 2632.84 (11) \text{ \AA}^3$
$M_r = 574.98$	$Z = 4$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 9.0206 (2) \text{ \AA}$	$\mu = 1.08 \text{ mm}^{-1}$
$b = 16.7979 (4) \text{ \AA}$	$T = 294 \text{ K}$
$c = 17.3754 (5) \text{ \AA}$	$0.35 \times 0.30 \times 0.23 \text{ mm}$

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer	40587 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	3311 independent reflections
$T_{\min} = 0.69, T_{\max} = 0.78$	2614 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	155 parameters
$wR(F^2) = 0.116$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\max} = 0.58 \text{ e \AA}^{-3}$
3311 reflections	$\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$

Structure (I) posed some problems due to disorder. Water molecule O1W appeared depleted and refinement of its site-occupancy factor converged to 0.60 (2). The perchlorate anion, in turn, appeared split into two almost 'mirror-related' parts with very different occupancies [0.922 (3) and 0.078 (3)]. Three O atoms in the major

Table 4
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...O2	0.91	2.31	3.188 (3)	161
N2—H2N...O4	0.91	2.54	3.403 (3)	159
N2—H2N...O1	0.91	2.48	3.099 (3)	126
C7—H7A...O1 ¹	0.96	2.42	3.295 (4)	151

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 5
Comparison of reported transition metal complexes with diastereomers of the *L* ligand and similar chiral sites.

CSD refcode (Reference)	Space group	Cation (symmetry)	Sequence (type)
DEFJIH (Lee <i>et al.</i> , 1985)	<i>P</i> ₂ / <i>c</i>	Cu ($\bar{1}$)	RRRR—SSSS (1)
OCMENH (Ferguson <i>et al.</i> , 1990)	<i>P</i> ₂ / <i>1</i> <i>n</i>	Ni ($\bar{1}$)	RRRR—SSSS (1)
POTPUJ (Hazari <i>et al.</i> , 1997)	<i>P</i> ₂ / <i>c</i>	Cu ($\bar{1}$)	RRRR—SSSS (1)
QOPJIO (Horn <i>et al.</i> , 2001)	<i>P</i> $\bar{1}$	Co ($\bar{1}$)	RRRR—SSSS (1)
(I) (this work)	<i>Pbca</i>	Cu ($\bar{1}$)	RRRR—SSSS (1)
(II) (this work)	<i>P</i> $\bar{1}$	Cu ($\bar{1}$)	RRRR—SSSS (1)
IDAQIP (Roy, Hazari, Barua & Tiekink, 2011)	<i>Pbca</i>	Zn (1)	SRRR—SSRS (2)
LIFHAJ (Choi & Suh, 1999)	<i>P</i> $\bar{1}$	Zn (1)	SRRR—SSRS (2)
YAVFOS (Roy <i>et al.</i> , 2012)	<i>C</i> ₂ / <i>c</i>	Cd (1)	SRRR—SSRS (2)
BAQHAC (Choi <i>et al.</i> , 1999)	<i>P</i> $\bar{1}$	Ni (1)	RSSR—RSSS (3)
MAKPOF (Roy <i>et al.</i> , 2010)	<i>C</i> ₂ / <i>c</i>	Cd (1)	RSSR—RSSS (3)
ECUREA (Lin <i>et al.</i> , 2006)	<i>P</i> ₂ <i>1</i> ₂ <i>1</i>	Ni (1)	SSSR—SSRS (4)
(III) (Lin <i>et al.</i> , 2006)	<i>P</i> ₂ / <i>c</i>	Cu (1)	RRRS—RSRS (5)
EQOGIB (Roy, Hazari, Dey <i>et al.</i> , 2011)	<i>P</i> $\bar{1}$	Zn (1)	RRSR—RSSS (6)
OCMENI (Ito <i>et al.</i> , 1981)	<i>P</i> ₄ <i>3</i> ₂ <i>2</i>	Ni (1)	SSSR—SSSR (7)
VIVSUO (Bembi <i>et al.</i> , 1991)	<i>P</i> ₂ / <i>c</i>	Co ($\bar{1}$)	SRSR—RSRS (8)

component (O1, O2 and O4) appear relatively near their O1', O2' and O4' counterparts, and the least-squares plane through the six-membered group corresponds roughly to the 'mirror' relating the two components. The Cl atoms (Cl1 and Cl1') and the fourth O atoms (O3 and O3') lie on both sides, at 0.358 (2) and -0.372 (2) Å, and at 1.703 (3) and -1.708 (3) Å, respectively, from the plane.

Due to the very small site-occupancy factor for the minor component [0.078 (2)], strong similarity restraints (in both metrics and displacement factors) were introduced in order to link them to the corresponding parameters in the major component.

C- and N-bound H atoms were found in a difference map, further idealized and finally allowed to ride. Methyl groups were also free to rotate. Water H atoms in (I) were difficult to find, due to depletion, but the hydrogen-bonding donor–acceptor scheme for O1W clearly defined a restrained solid angle for them. The inclusion of an idealized water molecule (O—H = 0.85 Å and H...H = 1.35 Å) resulted in the H atoms lying in slightly positive zones in the difference Fourier map and involved in strong hydrogen bonding. The final positions came from a restrained refinement, with O—H = 0.85 (1) Å and H...H = 1.35 (1) Å. In all cases, H-atom displacement parameters were taken as $U_{iso}(H) = kU_{eq}(host)$, with C—H = 0.96 Å and $k = 1.5$ for methyl H atoms, C—H = 0.93 Å and $k = 1.2$ for aromatic H atoms, N—H = 0.85 Å and $k = 1.2$, and O—H = 0.85 Å and $k = 1.5$.

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008);

software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3486). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2013). C69, 689-695 [doi:10.1107/S0108270113013711]

Two solvatomorphic forms of a copper complex formulated as $\text{Cu}(L^1)(\text{ClO}_4)_2 \cdot 1.2\text{H}_2\text{O}$ and $\text{Cu}(L^1)(\text{ClO}_4)_2$, where L^1 is 3,10-C-meso-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane

Babul Chandra Nath, Sebastián Suarez, Fabio Doctorovich, Tapashi G. Roy and Ricardo Baggio

Computing details

For both compounds, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

(I) (3,10-C-meso-3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradecane)bis(perchlorato- κO)copper(II) 1.2-hydrate

Crystal data

$[\text{Cu}(\text{ClO}_4)_2(\text{C}_{18}\text{H}_{40}\text{N}_4)] \cdot 1.2\text{H}_2\text{O}$
 $M_r = 596.61$
 Triclinic, $P\bar{1}$
 Hall symbol: $-P\ 1$
 $a = 8.5783$ (10) Å
 $b = 8.7819$ (12) Å
 $c = 10.2156$ (13) Å
 $\alpha = 114.835$ (13)°
 $\beta = 98.036$ (10)°
 $\gamma = 98.616$ (11)°
 $V = 672.67$ (17) Å³

$Z = 1$
 $F(000) = 315.0$
 $D_x = 1.473$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2039 reflections
 $\theta = 3.7\text{--}29.0^\circ$
 $\mu = 1.06$ mm⁻¹
 $T = 294$ K
 Block, red
 $0.35 \times 0.25 \times 0.20$ mm

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans, thick slices
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.72$, $T_{\max} = 0.82$

9475 measured reflections
 3193 independent reflections
 2285 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\text{max}} = 29.1^\circ$, $\theta_{\text{min}} = 3.7^\circ$
 $h = -11 \rightarrow 11$
 $k = -11 \rightarrow 11$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.170$

$S = 0.93$

3193 reflections

183 parameters

97 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0891P)^2 + 0.8414P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.73 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.5000	0.5000	0.5000	0.0396 (2)	
N1	0.4193 (4)	0.4998 (4)	0.3045 (3)	0.0432 (7)	
H1N	0.4850	0.4473	0.2459	0.052*	
N2	0.3720 (4)	0.2576 (4)	0.4358 (3)	0.0399 (7)	
H2N	0.4379	0.1906	0.3899	0.048*	
C1	0.4601 (5)	0.6810 (5)	0.3304 (5)	0.0516 (9)	
H1A	0.3821	0.7410	0.3777	0.062*	
H1B	0.4557	0.6853	0.2367	0.062*	
C2	0.2487 (5)	0.4023 (5)	0.2150 (5)	0.0518 (10)	
C3	0.2286 (5)	0.2165 (5)	0.1939 (4)	0.0499 (9)	
H3A	0.1324	0.1470	0.1163	0.060*	
H3B	0.3201	0.1750	0.1574	0.060*	
C4	0.2151 (4)	0.1818 (5)	0.3250 (4)	0.0435 (8)	
H4	0.1333	0.2381	0.3713	0.052*	
C5	0.3710 (5)	0.2314 (5)	0.5712 (4)	0.0462 (9)	
H5	0.3524	0.1075	0.5421	0.055*	
C6	0.2299 (9)	0.3967 (8)	0.0608 (6)	0.094 (2)	
H6A	0.3201	0.3615	0.0201	0.141*	
H6B	0.2265	0.5092	0.0694	0.141*	
H6C	0.1313	0.3159	-0.0031	0.141*	
C7	0.1256 (5)	0.4880 (6)	0.2930 (7)	0.0729 (15)	
H7A	0.0217	0.4085	0.2532	0.109*	
H7B	0.1192	0.5881	0.2783	0.109*	
H7C	0.1579	0.5218	0.3969	0.109*	
C8	0.1590 (5)	-0.0120 (5)	0.2735 (5)	0.0593 (11)	
H8A	0.0548	-0.0546	0.2064	0.089*	
H8B	0.1516	-0.0330	0.3576	0.089*	
H8C	0.2354	-0.0700	0.2240	0.089*	
C9	0.2394 (6)	0.2996 (6)	0.6470 (5)	0.0617 (11)	

H9A	0.2454	0.4158	0.6614	0.093*	
H9B	0.2539	0.2979	0.7413	0.093*	
H9C	0.1355	0.2284	0.5865	0.093*	
O1W	0.5853 (11)	0.2881 (8)	0.0354 (8)	0.094 (3)	0.60 (2)
H1WB	0.519 (13)	0.197 (9)	−0.031 (10)	0.141*	0.60 (2)
H1WA	0.618 (16)	0.263 (14)	0.105 (9)	0.141*	0.60 (2)
Cl1	0.72465 (13)	0.12868 (15)	0.28330 (15)	0.0532 (4)	0.922 (3)
O3	0.8372 (4)	0.1240 (5)	0.3979 (4)	0.0814 (12)	0.922 (3)
O1	0.6966 (7)	0.2981 (5)	0.3343 (6)	0.0854 (12)	0.922 (3)
O2	0.7911 (5)	0.0887 (6)	0.1564 (4)	0.0908 (14)	0.922 (3)
O4	0.5759 (4)	0.0117 (5)	0.2537 (5)	0.0791 (13)	0.922 (3)
Cl1'	0.7019 (16)	0.1550 (18)	0.2246 (19)	0.0532 (4)	0.078 (3)
O3'	0.699 (4)	0.191 (5)	0.101 (3)	0.0814 (12)	0.078 (3)
O1'	0.684 (6)	0.302 (4)	0.348 (4)	0.0854 (12)	0.078 (3)
O2'	0.852 (3)	0.115 (6)	0.261 (4)	0.0908 (14)	0.078 (3)
O4'	0.572 (4)	0.012 (5)	0.189 (5)	0.0791 (13)	0.078 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0338 (3)	0.0382 (4)	0.0424 (4)	0.0018 (2)	0.0053 (2)	0.0174 (3)
N1	0.0450 (17)	0.0383 (16)	0.0443 (17)	0.0071 (13)	0.0103 (13)	0.0174 (13)
N2	0.0370 (15)	0.0378 (16)	0.0435 (16)	0.0080 (12)	0.0115 (12)	0.0166 (13)
C1	0.053 (2)	0.048 (2)	0.051 (2)	0.0045 (18)	0.0040 (18)	0.0253 (19)
C2	0.048 (2)	0.050 (2)	0.047 (2)	0.0023 (17)	−0.0038 (17)	0.0198 (18)
C3	0.047 (2)	0.045 (2)	0.043 (2)	0.0026 (16)	0.0026 (16)	0.0114 (17)
C4	0.0391 (19)	0.0356 (18)	0.047 (2)	0.0038 (14)	0.0083 (15)	0.0124 (16)
C5	0.048 (2)	0.0383 (19)	0.051 (2)	0.0022 (16)	0.0088 (17)	0.0227 (17)
C6	0.118 (5)	0.083 (4)	0.057 (3)	−0.019 (3)	−0.022 (3)	0.037 (3)
C7	0.042 (2)	0.054 (3)	0.106 (4)	0.011 (2)	0.001 (2)	0.026 (3)
C8	0.050 (2)	0.040 (2)	0.070 (3)	−0.0036 (17)	0.002 (2)	0.017 (2)
C9	0.063 (3)	0.066 (3)	0.054 (2)	0.002 (2)	0.020 (2)	0.026 (2)
O1W	0.132 (7)	0.065 (4)	0.076 (5)	0.012 (4)	0.015 (4)	0.030 (4)
Cl1	0.0441 (6)	0.0503 (6)	0.0659 (8)	0.0112 (4)	0.0200 (5)	0.0243 (6)
O3	0.064 (2)	0.091 (3)	0.087 (3)	0.017 (2)	0.005 (2)	0.042 (2)
O1	0.081 (3)	0.058 (2)	0.122 (3)	0.0243 (18)	0.042 (2)	0.037 (2)
O2	0.094 (3)	0.111 (4)	0.069 (3)	0.035 (3)	0.042 (2)	0.031 (3)
O4	0.055 (2)	0.071 (2)	0.109 (4)	0.0029 (17)	0.016 (2)	0.043 (3)
Cl1'	0.0441 (6)	0.0503 (6)	0.0659 (8)	0.0112 (4)	0.0200 (5)	0.0243 (6)
O3'	0.064 (2)	0.091 (3)	0.087 (3)	0.017 (2)	0.005 (2)	0.042 (2)
O1'	0.081 (3)	0.058 (2)	0.122 (3)	0.0243 (18)	0.042 (2)	0.037 (2)
O2'	0.094 (3)	0.111 (4)	0.069 (3)	0.035 (3)	0.042 (2)	0.031 (3)
O4'	0.055 (2)	0.071 (2)	0.109 (4)	0.0029 (17)	0.016 (2)	0.043 (3)

Geometric parameters (\AA , $^\circ$)

Cu1—N1 ⁱ	2.020 (3)	C5—C1 ⁱ	1.520 (6)
Cu1—N1	2.020 (3)	C5—H5	0.9800
Cu1—N2 ⁱ	2.023 (3)	C6—H6A	0.9600

Cu1—N2	2.023 (3)	C6—H6B	0.9600
Cu1—O1 ⁱ	2.833 (4)	C6—H6C	0.9600
Cu1—O1	2.833 (4)	C7—H7A	0.9600
N1—C1	1.476 (5)	C7—H7B	0.9600
N1—C2	1.518 (5)	C7—H7C	0.9600
N1—H1N	0.9100	C8—H8A	0.9600
N2—C4	1.486 (5)	C8—H8B	0.9600
N2—C5	1.496 (5)	C8—H8C	0.9600
N2—H2N	0.9100	C9—H9A	0.9600
C1—C5 ⁱ	1.520 (6)	C9—H9B	0.9600
C1—H1A	0.9700	C9—H9C	0.9600
C1—H1B	0.9700	O1W—H1WB	0.850 (10)
C2—C7	1.511 (7)	O1W—H1WA	0.851 (10)
C2—C3	1.532 (6)	C11—O2	1.418 (3)
C2—C6	1.539 (6)	C11—O3	1.428 (3)
C3—C4	1.509 (5)	C11—O4	1.419 (3)
C3—H3A	0.9700	C11—O1	1.427 (3)
C3—H3B	0.9700	C11'—O3'	1.422 (4)
C4—C8	1.528 (5)	C11'—O4'	1.423 (4)
C4—H4	0.9800	C11'—O2'	1.422 (4)
C5—C9	1.513 (6)	C11'—O1'	1.423 (4)
N1 ⁱ —Cu1—N2 ⁱ	94.25 (12)	C3—C4—H4	108.2
N1—Cu1—N2 ⁱ	85.75 (12)	C8—C4—H4	108.2
N1 ⁱ —Cu1—N2	85.75 (12)	N2—C5—C9	112.1 (3)
N1—Cu1—N2	94.25 (12)	N2—C5—C1 ⁱ	105.9 (3)
N1 ⁱ —Cu1—O1 ⁱ	81.43 (14)	C9—C5—C1 ⁱ	113.0 (4)
N1—Cu1—O1 ⁱ	98.57 (14)	N2—C5—H5	108.6
N2 ⁱ —Cu1—O1 ⁱ	78.20 (13)	C9—C5—H5	108.6
N2—Cu1—O1 ⁱ	101.80 (13)	C1 ⁱ —C5—H5	108.6
N1 ⁱ —Cu1—O1	98.57 (14)	C2—C6—H6A	109.5
N1—Cu1—O1	81.43 (14)	C2—C6—H6B	109.5
N2 ⁱ —Cu1—O1	101.80 (13)	H6A—C6—H6B	109.5
N2—Cu1—O1	78.20 (13)	C2—C6—H6C	109.5
C1—N1—C2	114.2 (3)	H6A—C6—H6C	109.5
C1—N1—Cu1	106.5 (2)	H6B—C6—H6C	109.5
C2—N1—Cu1	120.1 (2)	C2—C7—H7A	109.5
C1—N1—H1N	104.9	C2—C7—H7B	109.5
C2—N1—H1N	104.9	H7A—C7—H7B	109.5
Cu1—N1—H1N	104.9	C2—C7—H7C	109.5
C4—N2—C5	114.2 (3)	H7A—C7—H7C	109.5
C4—N2—Cu1	122.3 (2)	H7B—C7—H7C	109.5
C5—N2—Cu1	108.0 (2)	C4—C8—H8A	109.5
C4—N2—H2N	103.3	C4—C8—H8B	109.5
C5—N2—H2N	103.3	H8A—C8—H8B	109.5
Cu1—N2—H2N	103.3	C4—C8—H8C	109.5
N1—C1—C5 ⁱ	109.6 (3)	H8A—C8—H8C	109.5
N1—C1—H1A	109.8	H8B—C8—H8C	109.5
C5 ⁱ —C1—H1A	109.8	C5—C9—H9A	109.5

N1—C1—H1B	109.8	C5—C9—H9B	109.5
C5 ⁱ —C1—H1B	109.8	H9A—C9—H9B	109.5
H1A—C1—H1B	108.2	C5—C9—H9C	109.5
C7—C2—N1	110.6 (3)	H9A—C9—H9C	109.5
C7—C2—C3	111.7 (4)	H9B—C9—H9C	109.5
N1—C2—C3	107.4 (3)	H1WB—O1W—H1WA	105.1 (17)
C7—C2—C6	110.4 (5)	O2—Cl1—O3	109.2 (2)
N1—C2—C6	108.9 (4)	O2—Cl1—O4	112.4 (3)
C3—C2—C6	107.7 (4)	O3—Cl1—O4	108.8 (2)
C4—C3—C2	118.7 (3)	O2—Cl1—O1	109.4 (3)
C4—C3—H3A	107.6	O3—Cl1—O1	108.7 (3)
C2—C3—H3A	107.6	O4—Cl1—O1	108.3 (2)
C4—C3—H3B	107.6	Cl1—O1—Cu1	140.1 (3)
C2—C3—H3B	107.6	O3'—Cl1'—O4'	109.4 (5)
H3A—C3—H3B	107.1	O3'—Cl1'—O2'	109.6 (5)
N2—C4—C3	110.0 (3)	O4'—Cl1'—O2'	109.5 (5)
N2—C4—C8	112.1 (3)	O3'—Cl1'—O1'	109.5 (5)
C3—C4—C8	110.0 (3)	O4'—Cl1'—O1'	109.3 (5)
N2—C4—H4	108.2	O2'—Cl1'—O1'	109.5 (5)
N2 ⁱ —Cu1—N1—C1	-14.7 (3)	C5—N2—C4—C3	179.5 (3)
N2—Cu1—N1—C1	165.3 (3)	Cu1—N2—C4—C3	46.2 (4)
O1 ⁱ —Cu1—N1—C1	62.7 (3)	C5—N2—C4—C8	-57.7 (4)
O1—Cu1—N1—C1	-117.3 (3)	Cu1—N2—C4—C8	169.0 (3)
N2 ⁱ —Cu1—N1—C2	-146.4 (3)	C2—C3—C4—N2	-68.5 (4)
N2—Cu1—N1—C2	33.6 (3)	C2—C3—C4—C8	167.5 (4)
O1 ⁱ —Cu1—N1—C2	-69.0 (3)	C4—N2—C5—C9	-55.8 (4)
O1—Cu1—N1—C2	111.0 (3)	Cu1—N2—C5—C9	83.9 (3)
N1 ⁱ —Cu1—N2—C4	150.3 (3)	C4—N2—C5—Cl ⁱ	-179.4 (3)
N1—Cu1—N2—C4	-29.7 (3)	Cu1—N2—C5—Cl ⁱ	-39.8 (3)
O1 ⁱ —Cu1—N2—C4	70.0 (3)	O2—Cl1—O1—Cu1	155.8 (4)
O1—Cu1—N2—C4	-110.0 (3)	O3—Cl1—O1—Cu1	-85.0 (5)
N1 ⁱ —Cu1—N2—C5	14.6 (2)	O4—Cl1—O1—Cu1	33.1 (6)
N1—Cu1—N2—C5	-165.4 (2)	N1 ⁱ —Cu1—O1—Cl1	62.7 (5)
O1 ⁱ —Cu1—N2—C5	-65.7 (3)	N1—Cu1—O1—Cl1	-117.3 (5)
O1—Cu1—N2—C5	114.3 (3)	N2 ⁱ —Cu1—O1—Cl1	158.9 (5)
C2—N1—C1—C5 ⁱ	176.4 (3)	N2—Cu1—O1—Cl1	-21.1 (5)
Cu1—N1—C1—C5 ⁱ	41.5 (4)	O4'—Cl1'—O3'—O1'	119.8 (7)
C1—N1—C2—C7	-59.9 (5)	O2'—Cl1'—O3'—O1'	-120.1 (7)
Cu1—N1—C2—C7	68.5 (4)	O3'—Cl1'—O1'—O4'	119.8 (7)
C1—N1—C2—C3	178.1 (3)	O2'—Cl1'—O1'—O4'	-120.0 (7)
Cu1—N1—C2—C3	-53.6 (4)	O3'—Cl1'—O2'—O1'	120.1 (7)
C1—N1—C2—C6	61.6 (5)	O4'—Cl1'—O2'—O1'	-119.9 (7)
Cu1—N1—C2—C6	-170.0 (3)	O4'—O1'—O2'—Cl1'	35.3 (4)
C7—C2—C3—C4	-49.0 (5)	O3'—Cl1'—O4'—O1'	-119.9 (7)
N1—C2—C3—C4	72.3 (4)	O2'—Cl1'—O4'—O1'	119.9 (7)
C6—C2—C3—C4	-170.4 (4)		

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1N···O1 <i>W</i>	0.91	2.38	3.261 (9)	163
N2—H2N···O4	0.91	2.23	3.138 (6)	173
C7—H7C···O1 ⁱ	0.96	2.52	3.437 (7)	159
C9—H9A···O1 ⁱ	0.96	2.47	3.412 (7)	168
O1 <i>W</i> —H1 <i>WA</i> ···O2	0.85 (1)	2.44 (9)	3.137 (9)	139 (12)
O1 <i>W</i> —H1 <i>WA</i> ···O1	0.85 (1)	2.22 (4)	3.029 (9)	159 (11)
O1 <i>W</i> —H1 <i>WB</i> ···O4 ⁱⁱ	0.85 (1)	2.17 (6)	2.967 (8)	155 (12)

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

(II) (3,10-C-meso-3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradecane)bis(perchlorato- κ O)copper(II)

Crystal data

[Cu(ClO₄)₂(C₁₈H₄₀N₄)]

$M_r = 574.98$

Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

$a = 9.0206$ (2) Å

$b = 16.7979$ (4) Å

$c = 17.3754$ (5) Å

$V = 2632.84$ (11) Å³

$Z = 4$

$F(000) = 1212$

$D_x = 1.451$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 10594 reflections

$\theta = 3.8$ – 28.9°

$\mu = 1.08$ mm⁻¹

$T = 294$ K

Prism, blue

$0.35 \times 0.30 \times 0.23$ mm

Data collection

Oxford Gemini S Ultra CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans, thick slices

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.69$, $T_{\max} = 0.78$

40587 measured reflections

3311 independent reflections

2614 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 29.0^\circ$, $\theta_{\min} = 4.1^\circ$

$h = -12 \rightarrow 11$

$k = -22 \rightarrow 22$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.116$

$S = 1.07$

3311 reflections

155 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 2.9167P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.58$ e Å⁻³

$\Delta\rho_{\min} = -0.37$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.5000	0.5000	0.03007 (13)
N1	0.5404 (2)	0.52047 (11)	0.38696 (11)	0.0316 (4)
H1N	0.4785	0.4866	0.3617	0.038*
N2	0.3222 (2)	0.57382 (11)	0.50517 (10)	0.0322 (4)
H2N	0.2454	0.5424	0.4899	0.039*
C1	0.6913 (3)	0.48889 (16)	0.37144 (15)	0.0412 (6)
H1A	0.7651	0.5264	0.3897	0.049*
H1B	0.7050	0.4820	0.3165	0.049*
C2	0.5087 (3)	0.60077 (15)	0.35222 (14)	0.0377 (5)
C3	0.3492 (3)	0.62349 (15)	0.37188 (14)	0.0392 (5)
H3A	0.3224	0.6684	0.3397	0.047*
H3B	0.2862	0.5794	0.3567	0.047*
C4	0.3101 (3)	0.64493 (14)	0.45420 (15)	0.0410 (6)
H4	0.3791	0.6858	0.4724	0.049*
C5	0.2891 (3)	0.58991 (15)	0.58827 (14)	0.0379 (5)
H5	0.1849	0.6059	0.5927	0.046*
C6	0.5180 (4)	0.5943 (2)	0.26429 (17)	0.0628 (9)
H6A	0.6170	0.5797	0.2496	0.094*
H6B	0.4931	0.6446	0.2416	0.094*
H6C	0.4498	0.5544	0.2466	0.094*
C7	0.6183 (3)	0.66191 (16)	0.3822 (2)	0.0560 (8)
H7A	0.6257	0.6574	0.4371	0.084*
H7B	0.5848	0.7144	0.3689	0.084*
H7C	0.7138	0.6526	0.3595	0.084*
C8	0.1528 (4)	0.6789 (2)	0.4556 (2)	0.0660 (9)
H8A	0.0846	0.6398	0.4363	0.099*
H8B	0.1485	0.7257	0.4239	0.099*
H8C	0.1265	0.6926	0.5075	0.099*
C9	0.3847 (3)	0.65576 (17)	0.62169 (17)	0.0516 (7)
H9A	0.4870	0.6454	0.6101	0.077*
H9B	0.3716	0.6576	0.6765	0.077*
H9C	0.3561	0.7059	0.5997	0.077*
Cl1	0.16768 (7)	0.40599 (4)	0.38324 (4)	0.04963 (19)
O1	0.2652 (4)	0.40146 (17)	0.44882 (15)	0.0861 (8)
O2	0.2631 (3)	0.42568 (17)	0.31962 (14)	0.0775 (7)
O3	0.0934 (4)	0.33385 (16)	0.3735 (2)	0.0996 (10)
O4	0.0700 (3)	0.47002 (17)	0.3996 (2)	0.1034 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0301 (2)	0.0285 (2)	0.0316 (2)	0.00372 (15)	0.00700 (15)	-0.00055 (15)
N1	0.0297 (9)	0.0321 (9)	0.0329 (10)	-0.0021 (8)	0.0048 (8)	-0.0026 (8)
N2	0.0294 (9)	0.0301 (9)	0.0371 (10)	0.0012 (8)	0.0030 (8)	-0.0033 (7)
C1	0.0324 (12)	0.0490 (14)	0.0423 (13)	0.0026 (10)	0.0134 (10)	0.0010 (11)
C2	0.0400 (12)	0.0371 (12)	0.0361 (12)	-0.0021 (10)	0.0014 (10)	0.0054 (10)
C3	0.0397 (13)	0.0368 (12)	0.0410 (13)	0.0034 (10)	-0.0047 (10)	0.0049 (10)
C4	0.0437 (13)	0.0303 (11)	0.0489 (14)	0.0063 (10)	0.0034 (11)	0.0010 (10)
C5	0.0299 (11)	0.0416 (13)	0.0423 (13)	0.0068 (10)	0.0096 (10)	-0.0067 (10)
C6	0.068 (2)	0.083 (2)	0.0375 (15)	0.0095 (17)	0.0067 (14)	0.0124 (15)
C7	0.0481 (15)	0.0379 (14)	0.082 (2)	-0.0105 (12)	-0.0052 (15)	0.0052 (14)
C8	0.064 (2)	0.0592 (19)	0.075 (2)	0.0334 (16)	0.0099 (17)	0.0083 (16)
C9	0.0552 (16)	0.0449 (14)	0.0549 (16)	0.0080 (13)	-0.0023 (13)	-0.0181 (13)
C11	0.0419 (3)	0.0424 (3)	0.0646 (4)	-0.0072 (3)	-0.0027 (3)	0.0043 (3)
O1	0.100 (2)	0.0914 (19)	0.0664 (15)	-0.0083 (16)	-0.0196 (15)	0.0034 (14)
O2	0.0775 (16)	0.0961 (19)	0.0589 (13)	-0.0171 (14)	0.0028 (13)	0.0070 (13)
O3	0.093 (2)	0.0633 (16)	0.143 (3)	-0.0362 (15)	0.0096 (19)	-0.0193 (17)
O4	0.0609 (16)	0.0619 (15)	0.187 (3)	0.0083 (14)	0.0214 (19)	0.003 (2)

Geometric parameters (\AA , $^\circ$)

Cu1—N1	2.0270 (19)	C4—C8	1.530 (4)
Cu1—N1 ⁱ	2.0270 (19)	C4—H4	0.9800
Cu1—N2	2.0295 (19)	C5—C1 ⁱ	1.508 (4)
Cu1—N2 ⁱ	2.0295 (19)	C5—C9	1.518 (4)
Cu1—O1 ⁱ	2.831 (3)	C5—H5	0.9800
Cu1—O1	2.831 (3)	C6—H6A	0.9600
N1—C1	1.486 (3)	C6—H6B	0.9600
N1—C2	1.505 (3)	C6—H6C	0.9600
N1—H1N	0.9100	C7—H7A	0.9600
N2—C4	1.491 (3)	C7—H7B	0.9600
N2—C5	1.499 (3)	C7—H7C	0.9600
N2—H2N	0.9100	C8—H8A	0.9600
C1—C5 ⁱ	1.508 (3)	C8—H8B	0.9600
C1—H1A	0.9700	C8—H8C	0.9600
C1—H1B	0.9700	C9—H9A	0.9600
C2—C7	1.517 (4)	C9—H9B	0.9600
C2—C3	1.527 (3)	C9—H9C	0.9600
C2—C6	1.534 (4)	C11—O3	1.395 (2)
C3—C4	1.517 (3)	C11—O4	1.419 (3)
C3—H3A	0.9700	C11—O2	1.439 (2)
C3—H3B	0.9700	C11—O1	1.442 (3)
N1—Cu1—N1 ⁱ	180.000 (1)	H3A—C3—H3B	107.0
N1—Cu1—N2	94.66 (7)	N2—C4—C3	110.66 (19)
N1 ⁱ —Cu1—N2	85.34 (7)	N2—C4—C8	111.0 (2)
N1—Cu1—N2 ⁱ	85.34 (7)	C3—C4—C8	108.7 (2)
N1 ⁱ —Cu1—N2 ⁱ	94.66 (7)	N2—C4—H4	108.8

N2—Cu1—N2 ⁱ	180.0	C3—C4—H4	108.8
N1—Cu1—O1 ⁱ	94.06 (8)	C8—C4—H4	108.8
N1 ⁱ —Cu1—O1 ⁱ	85.94 (8)	N2—C5—C1 ⁱ	105.40 (18)
N2—Cu1—O1 ⁱ	102.72 (9)	N2—C5—C9	112.7 (2)
N2 ⁱ —Cu1—O1 ⁱ	77.28 (9)	C1 ⁱ —C5—C9	113.3 (2)
N1—Cu1—O1	85.94 (8)	N2—C5—H5	108.4
N1 ⁱ —Cu1—O1	94.06 (8)	C1 ⁱ —C5—H5	108.4
N2—Cu1—O1	77.28 (9)	C9—C5—H5	108.4
N2 ⁱ —Cu1—O1	102.72 (9)	C2—C6—H6A	109.5
O1 ⁱ —Cu1—O1	180.0	C2—C6—H6B	109.5
C1—N1—C2	114.89 (18)	H6A—C6—H6B	109.5
C1—N1—Cu1	106.25 (15)	C2—C6—H6C	109.5
C2—N1—Cu1	120.44 (14)	H6A—C6—H6C	109.5
C1—N1—H1N	104.5	H6B—C6—H6C	109.5
C2—N1—H1N	104.5	C2—C7—H7A	109.5
Cu1—N1—H1N	104.5	C2—C7—H7B	109.5
C4—N2—C5	114.40 (18)	H7A—C7—H7B	109.5
C4—N2—Cu1	121.41 (15)	C2—C7—H7C	109.5
C5—N2—Cu1	108.07 (14)	H7A—C7—H7C	109.5
C4—N2—H2N	103.6	H7B—C7—H7C	109.5
C5—N2—H2N	103.6	C4—C8—H8A	109.5
Cu1—N2—H2N	103.6	C4—C8—H8B	109.5
N1—C1—C5 ⁱ	109.66 (19)	H8A—C8—H8B	109.5
N1—C1—H1A	109.7	C4—C8—H8C	109.5
C5 ⁱ —C1—H1A	109.7	H8A—C8—H8C	109.5
N1—C1—H1B	109.7	H8B—C8—H8C	109.5
C5 ⁱ —C1—H1B	109.7	C5—C9—H9A	109.5
H1A—C1—H1B	108.2	C5—C9—H9B	109.5
N1—C2—C7	110.2 (2)	H9A—C9—H9B	109.5
N1—C2—C3	108.23 (19)	C5—C9—H9C	109.5
C7—C2—C3	111.6 (2)	H9A—C9—H9C	109.5
N1—C2—C6	109.0 (2)	H9B—C9—H9C	109.5
C7—C2—C6	110.7 (2)	O3—C11—O4	112.60 (19)
C3—C2—C6	107.0 (2)	O3—C11—O2	113.16 (18)
C4—C3—C2	119.3 (2)	O4—C11—O2	110.55 (18)
C4—C3—H3A	107.5	O3—C11—O1	110.10 (19)
C2—C3—H3A	107.5	O4—C11—O1	105.1 (2)
C4—C3—H3B	107.5	O2—C11—O1	104.72 (17)
C2—C3—H3B	107.5	C11—O1—Cu1	132.38 (16)
N2—Cu1—N1—C1	165.81 (15)	C1—N1—C2—C6	62.7 (3)
N2 ⁱ —Cu1—N1—C1	-14.19 (15)	Cu1—N1—C2—C6	-168.19 (19)
O1 ⁱ —Cu1—N1—C1	62.68 (16)	N1—C2—C3—C4	70.6 (3)
O1—Cu1—N1—C1	-117.32 (16)	C7—C2—C3—C4	-50.8 (3)
N2—Cu1—N1—C2	32.98 (17)	C6—C2—C3—C4	-172.1 (2)
N2 ⁱ —Cu1—N1—C2	-147.02 (17)	C5—N2—C4—C3	178.52 (19)
O1 ⁱ —Cu1—N1—C2	-70.15 (17)	Cu1—N2—C4—C3	46.0 (3)
O1—Cu1—N1—C2	109.85 (17)	C5—N2—C4—C8	-60.8 (3)
N1—Cu1—N2—C4	-29.46 (18)	Cu1—N2—C4—C8	166.7 (2)

N1 ⁱ —Cu1—N2—C4	150.54 (18)	C2—C3—C4—N2	-67.7 (3)
O1 ⁱ —Cu1—N2—C4	65.77 (18)	C2—C3—C4—C8	170.2 (2)
O1—Cu1—N2—C4	-114.23 (18)	C4—N2—C5—C1 ⁱ	-179.7 (2)
N1—Cu1—N2—C5	-164.56 (15)	Cu1—N2—C5—C1 ⁱ	-41.1 (2)
N1 ⁱ —Cu1—N2—C5	15.44 (15)	C4—N2—C5—C9	-55.6 (3)
O1 ⁱ —Cu1—N2—C5	-69.33 (15)	Cu1—N2—C5—C9	83.0 (2)
O1—Cu1—N2—C5	110.67 (15)	O3—Cl1—O1—Cu1	166.2 (2)
C2—N1—C1—C5 ⁱ	177.8 (2)	O4—Cl1—O1—Cu1	-72.3 (3)
Cu1—N1—C1—C5 ⁱ	42.0 (2)	O2—Cl1—O1—Cu1	44.3 (3)
C1—N1—C2—C7	-59.0 (3)	N1—Cu1—O1—Cl1	-33.1 (2)
Cu1—N1—C2—C7	70.1 (2)	N1 ⁱ —Cu1—O1—Cl1	146.9 (2)
C1—N1—C2—C3	178.7 (2)	N2—Cu1—O1—Cl1	62.6 (2)
Cu1—N1—C2—C3	-52.2 (2)	N2 ⁱ —Cu1—O1—Cl1	-117.4 (2)

Symmetry code: (i) -x+1, -y+1, -z+1.

Hydrogen-bond geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1N...O2	0.91	2.31	3.188 (3)	161
N2—H2N...O4	0.91	2.54	3.403 (3)	159
N2—H2N...O1	0.91	2.48	3.099 (3)	126
C7—H7A...O1 ⁱ	0.96	2.42	3.295 (4)	151

Symmetry code: (i) -x+1, -y+1, -z+1.

Comparison of reported structures having the same L ligand and similar chiral sites

CSD refode (Reference)	Space group	Cation (symmetry)	Sequence (type)
DEFJIH (Lee <i>et al.</i> , 1985)	P2 ₁ /c	Cu ($\bar{1}$)	RRRR—SSSS (1)
OCMENH (Ferguson <i>et al.</i> , 1990)	P2 ₁ /n	Ni ($\bar{1}$)	RRRR—SSSS (1)
POTPUJ (Hazari <i>et al.</i> , 1997)	P2 ₁ /c	Cu ($\bar{1}$)	RRRR—SSSS (1)
QOPJIO (Horn <i>et al.</i> , 2001)	P $\bar{1}$	Co ($\bar{1}$)	RRRR—SSSS (1)
(I) (this work)	Pbca	Cu ($\bar{1}$)	RRRR—SSSS (1)
(II) (this work)	P $\bar{1}$	Cu ($\bar{1}$)	RRRR—SSSS (1)
IDAQIP (Roy, Hazari, Barua & Tiekink, 2011)	Pbca	Zn (1)	SRRR—SSRS (2)
LIFHAJ (Choi & Suh, 1999)	P $\bar{1}$	Zn (1)	SRRR—SSRS (2)
YAVFOS (Roy <i>et al.</i> , 2012)	C2/c	Cd (1)	SRRR—SSRS (2)
BAQHAC (Choi <i>et al.</i> , 1999)	P $\bar{1}$	Ni (1)	RSSR—RSSS (3)
MAKPOF (Roy <i>et al.</i> , 2010)	C2/c	Cd (1)	RSSR—RSSS (3)
ECUREA (Lin <i>et al.</i> , 2006)	P2 ₁ 2 ₁ 2 ₁	Ni (1)	SSSR—SSRS (4)
(III) (Lin <i>et al.</i> , 2006)	P2 ₁ /c	Cu (1)	RRRS—SRSR (5)
EQOGIB (Roy, Hazari, Dey <i>et al.</i> , 2011)	P $\bar{1}$	Zn (1)	RRSR—RSSS (6)
OCMENI (Ito <i>et al.</i> , 1981)	P4 ₃ 2 ₁ 2	Ni (1)	SSSR—SSSR (7)
VIVSUO (Bembi <i>et al.</i> , 1991)	P2 ₁ /c	Co ($\bar{1}$)	SRSR—SRSR (8)