Total Spontaneous Resolution of Chiral Covalent Networks from Stereochemically Labile Metal Complexes

Anna Johansson,[a] Mikael Håkansson,*[a] and Susan Jagner*[b]

Abstract: Stereochemically labile copper and zinc complexes with the *N*,*N*′-dimethylethylenediamine ligand (dmeda) have been shown to be promising precursors for the total spontaneous resolution of chiral covalent networks. (*N*,*N*′)-[Cu(NO$_3$)$_2$(dmeda)]$_\infty$ crystallises as a conglomerate and yields either enantiopure (*R*,*R*)-**1** or enantiopure (*S*,*S*)-**1**. A mixed-valence copper(I/II) complex, [{Cu^{II}Br$_2$-(dmeda)}$_3$(Cu^{I}Br)$_2$]$_\infty$ (**2**), which crystallises as a pair of interpenetrating chiral (10,3)-*a* nets, is formed from CuBr, CuBr$_2$ and dmeda. One net contains ligands with solely (*R*,*R*) configuration and exhibits helices with (*P*) configuration while the other has solely (*S*,*S*)-dmeda ligands and gives rise to a net in which the helices have (*M*) configuration. The whole crystalline arrangement is racemic, because the interpenetrating chiral nets are of opposite handedness. With zinc chloride (*R*,*S*)-[ZnCl(dmeda)$_2$]$_2$[ZnCl$_4$] (**3**) is obtained, which is a network structure, although not chiral. Total spontaneous resolution of stereochemically labile metal complexes formed from achiral or racemic building blocks is suggested as a viable route for the preparation of covalent chiral networks. Once the absolute structure of the compound has been determined by X-ray crystallography, a quantitative determination of the enantiomeric excess of the bulk product can be undertaken by means of solid-state CD spectroscopy.

Keywords: chiral networks · chiral resolution · circular dichroism · crystal engineering · mixed-valent compounds

Introduction

Recently, total spontaneous resolution of seven-coordinate and eight-coordinate transition metal complexes has been reported.[1,2] Owing to the stereochemical lability of these complexes in solution and hence their tendency to enantiomerise rapidly in solution, conventional solution-based methods for resolution of such enantiomers are ineffective. If, however, the complex crystallises as a conglomerate, it may undergo crystallisation-induced asymmetric transformation, also known as total spontaneous resolution.[3–5] A prerequisite for total spontaneous resolution, and, consequently, an enantiomerically enriched bulk product, is that the metal complex is stereochemically labile and is thus transformed into the relevant enantiomer as crystal nucleation proceeds. Although it is possible to determine the absolute configuration of a single crystal of an enantiomorph so formed by means of crystal structure determination, quantitative determination of the enantiomeric excess (*ee*) of a bulk product by this method would be extremely time-consuming and, if the bulk product is microcrystalline, hardly feasible. Solid-state CD spectroscopy has been exploited to solve this problem and has proven to be a powerful tool for quantitative *ee* determination of bulk samples.[2]

In previous investigations, we have studied the complexation of N-donor ligands with copper(I), and, in particular with enantiopure N-donor ligands. Thus, the first complexes between copper(I) chloride and (−)-sparteine have been prepared and characterised.[6] Another approach to the preparation of enantiopure complexes is the reaction between amines with a chirogenic N-centre and various metal ions.[7–9] A ligand with chirogenic N-donor atoms, *N*,*N*′-dimethylethylenediamine (dmeda) was selected for the present investigation. The ligand itself is not optically active in solution owing to rapid inversion at the nitrogen centre. When coordinated by a metal centre, however, a stereochemically labile complex is formed which enantiomerises in solution but can be optically active in the solid state. If the metal

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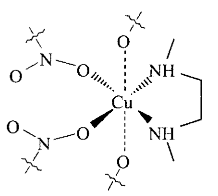
complex crystallises as a conglomerate, it ought to be possible to obtain an enantiopure product from the achiral (or racemic) building blocks by total spontaneous resolution. Thus, we envisaged that enantiopure chiral networks might be prepared by such a method, which was a primary objective of this work.

Given our previous investigations,[6,8,9] it was of interest to examine the behaviour of dmeda towards copper(I) and copper(II) halides and also zinc(II) chloride.[7,9] One of the enantiomers of the copper(II) nitrate complex with dmeda has been prepared and characterised earlier,[10] but (N,N')-[Cu(NO_3)$_2$(dmeda)] was included again in this investigation in order to examine the possibility of total spontaneous resolution of enantiomorphs. The results of this investigation are presented below, those compounds obtained being summarised below.



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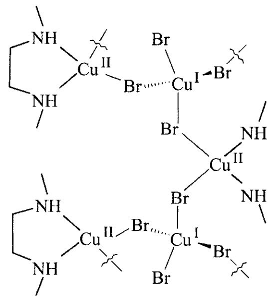

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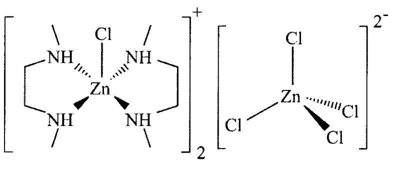

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Results and Discussion

Total spontaneous resolution of (N,N')-[Cu(NO_3)$_2$(dmeda)]$_\infty$: Compounds (*R*,*R*)-**1** and (*S*,*S*)-**1** have been prepared by total spontaneous resolution from copper(II) nitrate and the chelating amine dimethylethylenediamine (dmeda) which possesses chirogenic N-donors. The compound itself is not new,[10] but total spontaneous resolution into the (*R*,*R*) and (*S*,*S*) enantiomorphs has not been demonstrated previously. Nor has it been recognised that crystals of [Cu(NO_3)$_2$(dmeda)]$_\infty$ form a conglomerate, that is, the (*R*,*R*) and (*S*,*S*) enantiomers crystallise separately. As is seen from the solid-state CD spectra of (*R*,*R*)-**1** and (*S*,*S*)-**1** (Figure 1) and the calibration plot for quantitative *ee* determination[2] of the bulk material and single crystals (Figure 2), the products are essentially enantiopure. Thus, since the crystallisation starts without seeding and yields an enantiomerically enriched product, the preparation may be regarded as absolute asymmetric synthesis. Without seeding four of seven crystallisation experiments resulted in batches of enantiopure (*R*,*R*)-**1**. This implies a stochastic distribution of handedness in experiments in which crystallisation proceeds without seeding, in contrast to recently reported results.[11] Seeding can, of course, be used to predetermine which enantiomorph is formed. The usefulness of solid-state CD spectroscopy as a tool for quantitative *ee* determination and thus for assessing total spontaneous resolution of the bulk product,[2] has been further demonstrated here.

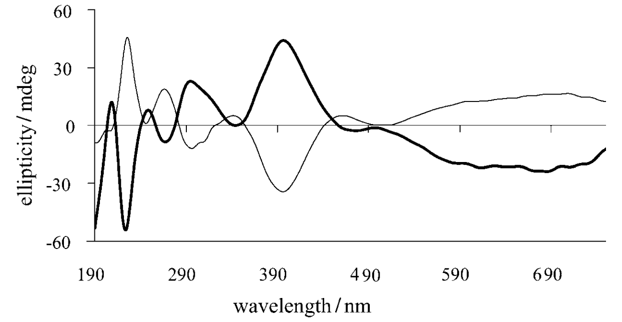

Figure 1. Solid-state CD spectra of (*R*,*R*)-**1** (bold) and (*S*,*S*)-**1**.

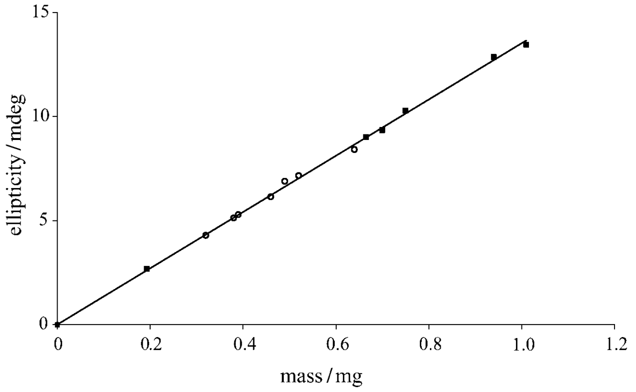

Figure 2. Enantiopure crystal mass of (*S*,*S*)-**1** is directly proportional to the magnitude of the CD signal. ■ represent the calibration line, constructed from enantiopure single crystals; ○ bulk product *ee* determinations, which show that the bulk product is essentially enantiopure.

The molecular structure of (N,N')-[Cu(NO_3)$_2$(dmeda)]$_\infty$ has been described previously and the connectivity relationships provided by this study (Table 1, Figure 3) are in good agreement with the those obtained in the previous determination.[10] If, however, the long coordinative bonds of 2.641(3) Å [(*R*,*R*)-**1**] and 2.637(3) Å [(*S*,*S*)-**1**)], which result in distorted octahedral coordination geometry for copper(II) (see also ref. [8]) are taken into account, the compounds may be considered to form three-dimensional networks (cf. Figure 4). Despite the chirality of the compounds themselves, the topology of the nets, in which copper(II) forms the nodes, can be described as (6,4), that is, diamondoid, which is achiral.

Table 1. Selected bond lengths [Å] for (*R*,*R*)-$[Cu(NO_3)_2(dmeda)]_\infty$ and (*S*,*S*)-$[Cu(NO_3)_2(dmeda)]_\infty$.[a]

(*R*,*R*)-**1**		(*S*,*S*)-**1**	
Cu1−O1	1.984(2)	Cu1−O1	1.987(2)
Cu1−N2	1.998(2)	Cu1−N2	1.994(2)
Cu1−O2^{i}	2.641(3)	Cu1−O2^{iii}	2.637(3)
O1−N1	1.280(4)	O1−N1	1.270(3)
N1−O2	1.238(3)	N1−O2	1.235(3)
N1−O3	1.203(4)	N1−O3	1.218(4)
N2−C1	1.459(4)	N2−C1	1.463(4)
N2−C2	1.473(4)	N2−C2	1.478(4)
C2−C2^{ii}	1.514(8)	C2−C2^{iv}	1.516(7)

[a] Symmetry code: i: $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{4}-z$; ii: $y, x, -z$; iii: $1\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{4}-z$; iv: $1-y, 1-x, \frac{1}{2}-z$.

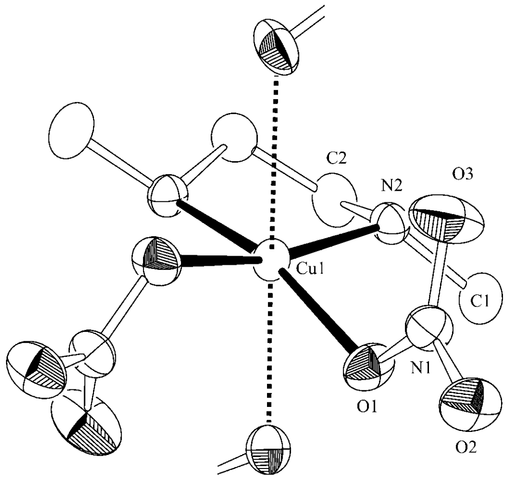

Figure 3. Molecular structure of (*S*,*S*)-**1**, showing the crystallographic numbering. Hydrogen atoms have been omitted. The structure of (*R*,*R*)-**1** is analogous. The long Cu1···O2 bonds of 2.64 Å have been drawn as broken lines.

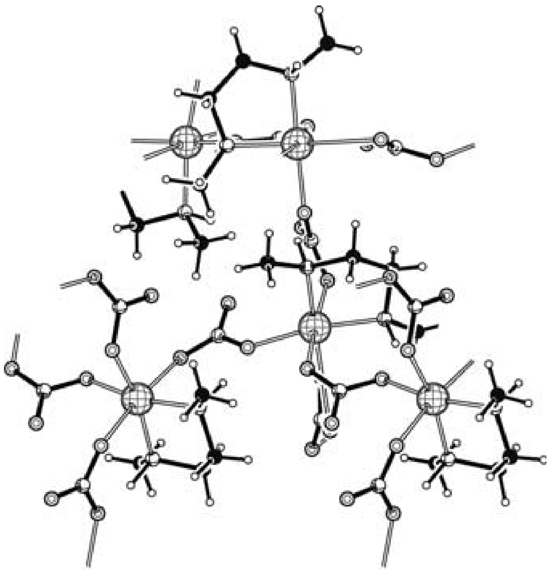

Figure 4. Part of the network formed by (*S*,*S*)-**1**.

$[\{Cu^{II}Br_2(dmeda)\}_3(Cu^{I}Br)_2]_\infty$ (2): A mixed-valence copper(I/II) complex was formed from copper(I) bromide and dmeda, single crystals of better quality being formed by mixing the copper(I) and copper(II) constituents. The N donors of the chelating dmeda ligand are coordinated as either both (*R*,*R*) or both (*S*,*S*). Compound **2** crystallises in the acentric space group $I\bar{4}3d$, but, owing to the presence of the glide plane, a conglomerate cannot be formed. Instead, **2** crystallises as a pair of enantiomorphic networks which are related by the *d*-glide plane. The structure of **2** can also be described as interpenetrating chiral nets of topology (10,3)-*a*,[12–17] in which the nodes are composed solely of the copper(I) centres. Part of a chiral net is illustrated in Figure 5. The topology of interpenetration of the chiral (10,3)-*a* nets is illustrated in Figure 6, where only the copper(I) nodes are depicted. One net contains ligands with solely (*R*,*R*) configuration and exhibits helices with (*P*) configuration while the other has solely (*S*,*S*)-dmeda ligands and gives rise to a net in which the helices have (*M*) configuration. It is possible that the chiral nets are stabilised by the presence of chiral ligands, even though the nets themselves do not require these groups for their definition. The whole crystalline arrangement is racemic,[12–14] since the interpenetrating chiral nets are of opposite handedness.

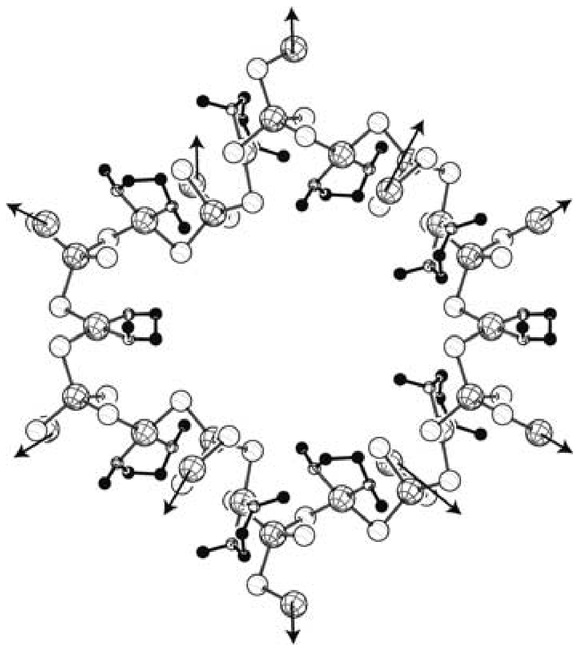

Figure 5. Ten-membered ring in the (10,3)-*a* net in **2**. Arrows indicate network expansion.

Several polymeric mixed-valence copper(I/II) compounds crystallise with one-dimensional,[18–20] two-dimensional[21–24] and three-dimensional arrays,[21–27] but there seem to be few examples of interpenetration[24,25] and few in which the network is built up primarily from covalent bonds[21,24–26] rather than weak interactions. Even examples of covalent interpenetrating (10,3)-*a* networks with other transition metals

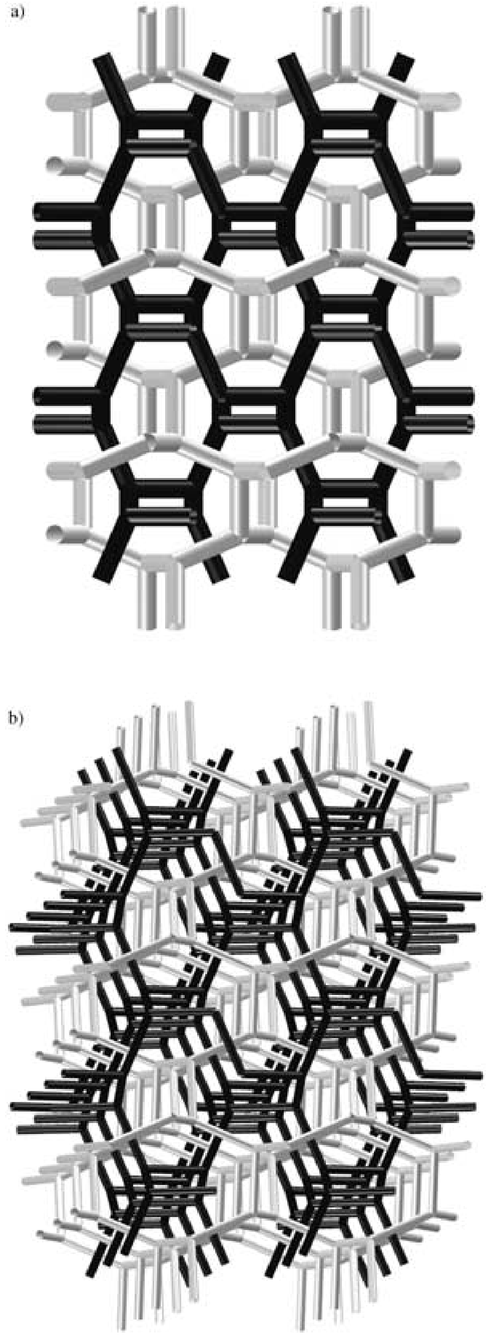

Figure 6. Showing a) the topology of the interpenetrating nets in **2** along the *c* axis, and b) how the (*R*,*R*) net (drawn in black) forms exclusively right-handed (*P*) helices.

appear to be somewhat scarce.[12,14] The novelty of **2** lies in its uniqueness as a chiral covalent interpenetrating mixed-valence copper(I/II) network with an uncommon topology.

The molecular structure of **2** is illustrated in Figure 7, showing the crystallographic numbering. Selected bond lengths and angles are given in Table 2. Copper(II) has essentially square-planar coordination geometry, whereas copper(I) exhibits a distorted tetrahedral coordination environment with one terminal and three bridging bromide ligands.

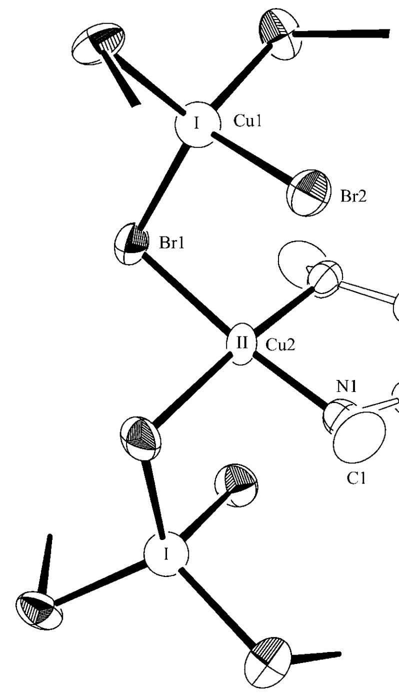

Figure 7. ORTEP drawing of **2**, showing the crystallographic numbering. Hydrogen atoms have been omitted.

Table 2. Selected bond lengths [Å] and angles [°] for $[\{Cu^{II}Br_2(dmeda)\}_3(Cu^{I}Br)_2]_\infty$ (**2**).[a]

Cu1−Br1	2.458(1)	Cu2−Br1	2.422(1)
Cu1−Br2	2.484(2)	Cu2−N1	2.011(5)
N1−C1	1.467(9)	Cu1···Cu2	3.586(1)
N1−C2a	1.46(1)	N1−C2b	1.53(2)
C2a−C2a^{i}	1.49(4)	C2b−C2b^{i}	1.51(4)
Br1-Cu1-Br1^{ii}	114.01(3)	N1-Cu2-N1^{i}	85.0(3)
Br1-Cu1-Br2	104.42(4)	N1-Cu2-Br1	173.7(2)
Br1-Cu2-Br1^{i}	91.49(5)	N1^{i}-Cu2-Br1	92.0(1)
Cu1-Br1-Cu2	94.60(4)		

[a] Symmetry code: i: $^1/_2-x$, y, $-z$; ii: y, z, x.

The dmeda ligand is bonded solely to copper(II) and both conformations of the five-membered chelating ring are present, resulting in crystallographic disorder associated with C2, this atom being successfully resolved into two components: C2a and C2b.

Since the metal centres are clearly discernible in terms of their coordination geometry, $[\{Cu^{II}(dmeda)Br_2\}_3(Cu^{I}Br)_2]$ (**2**) is perhaps best characterised as a Robin and Day[28] class I mixed-valence species. The dark reddish-brown colour of the compound indicates, however, some transfer of charge between the copper centres, which would suggest borderline class II behaviour, electron delocalisation probably being mediated by the bridging bromide ligands.[28] This phenomenon has also been demonstrated by Sherwood and Hoffmann[29] to occur in a mixed-valence Cu^{I}/Cu^{II} chlorocuprate reported by Willett.[30] Charge-transfer spectra in mixed-valence copper(I,II) species have been examined in some detail.[31,32] Unfortunately, the solid-state UV/visible spectrum for **2** lacked discrete features, preventing meaningful comparison with previous studies.[31,32] Solid-state measurements were necessary since the compound is insoluble in all common solvents and, moreover, it is not likely that the network structure of **2** is retained in solution.

Compound **2**, in which the harder N-donors are bonded to copper(II) and the softer bromide ligands to copper(I) is analogous, in this respect, to a novel mixed-valence trinuclear phenoxide.[33] In this latter complex, the central copper(II) is surrounded by O-donor ligands in a distorted square-planar arrangement whereas the softer peripheral copper(I) centres are each bonded to two alkene linkages and two oxide donors.[33] This compound, which is an even more striking example of the HSAB (hard and soft acids and bases) principle,[34] is also primarily a Robin and Day[28] class I mixed valence species, with its dark red colour indicating borderline class II behaviour. In recently prepared bromocuprate(I,II) species,[18,35] the copper centres are equivalent or nearly equivalent such that these compounds exhibit typical class III and class II behaviour with intermediate formal charges between one and two on the metal centres.[18,35] These bromocuprate(I) species share the property with **2** that the molecular motifs observed in the solid are unlikely to exist, as such, in the crystallising solution, but are assembled during crystal growth.[36] The relatively long Cu1···Cu2 distance of 3.586(1) Å in **2** is also indicative of class I behaviour. Typical class III behaviour would seem more often to result in shorter Cu···Cu distances of the order of 2.4 Å.[18,19] In the case of the polymeric $[Cu_2Br_5]^{2-}$ ion, however, the very short distance of 2.36 Å has been demonstrated to be associated with an energetically weak and soft Cu···Cu interaction.[18]

(*R*,*S*)-$[ZnCl(dmeda)_2]_2[ZnCl_4]$ (3): Selected bond lengths and angles for **3** are given in Table 3 and the crystallographic numbering of the chloro$(dmeda)_2$zinc(II) cation and tetrachlorozincate(II) anion is shown in Figure 8. Although the compound crystallises in an acentric space group, it is not chiral and does not crystallise as a conglomerate. Thus, both Zn1 and Cl1 are situated on a two-fold axis and the dmeda ligands are bonded to zinc in the *meso* mode such that the configuration of N1 is (*R*) whereas that of N2 is (*S*). Zn1 exhibits distorted square pyramidal coordination geometry with an apical chloride ligand and two dmeda groups forming the basal plane. The degree of trigonality, as expressed by the τ parameter,[37] is 0.28. It is interesting that in an analogous complex cation formed between (*R*,*R*)-bipyrrolidine and zinc(II) chloride, zinc exhibits trigonal bipyramidal coordination geometry with the chloride ligand situated in the trigonal plane.[38]

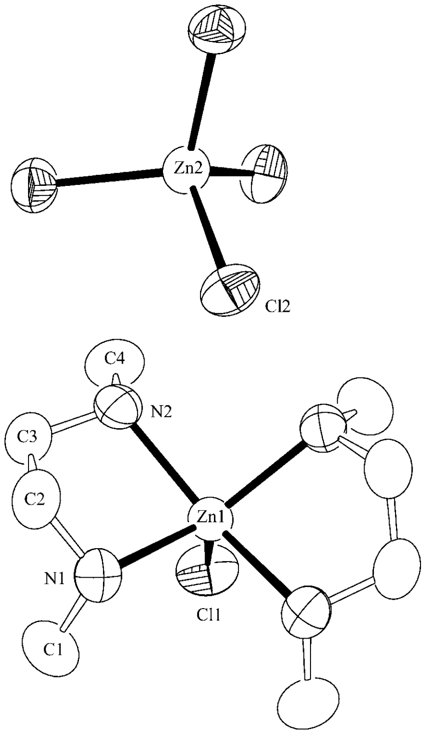

Figure 8. Constituent ions in **3** showing the crystallographic numbering. Hydrogen atoms have been omitted.

Table 3. Selected bond lengths [Å] and angles [°] for (*R*,*S*)-$[ZnCl(dmeda)_2]_2[ZnCl_4]$ (**3**).[a]

Zn1−Cl1	2.246(1)	Zn2−Cl2	2.2561(8)
Zn1−N1	2.159(2)	Zn1−N2	2.171(2)
N1−C1	1.476(4)	N2−C4	1.452(4)
N1−C2	1.458(4)	N2−C3	1.464(4)
C2−C3	1.497(5)		
Cl1-Zn1-N1	110.54(7)	Cl2-Zn2-Cl2^{i}	110.62(2)
Cl1-Zn1-N2	102.09(7)	Cl2-Zn2-Cl2^{ii}	107.19(4)
N1-Zn1-N2	80.7(1)	N1-Zn1-N1^{iii}	138.9(1)
N1-Zn1-N2^{iii}	90.8(1)	N2-Zn1-N2^{iii}	155.8(1)

[a] Symmetry code: i: $y, 1-x, 1-z$; ii: $1-x, 1-y, z$; iii: $\frac{1}{2}-x, y, \frac{3}{4}-z$.

The tetrachlorozincate(II) anion is comprised of Zn2 and Cl2, the former being situated on the $\bar{4}$ axis. There is a short contact of 2.5750(8) Å between Cl2 and H5 which links the structural motifs to form a three-dimensional network, illustrated in Figure 9, the topology of the net being (6,4), that is, diamondoid, with the zinc atoms of the chlorozincate(II) ion as nodes. Terminal metal-bound chlorine has been shown to be a good hydrogen-bond acceptor, in contrast to C–Cl counterparts.[39] Such hydrogen bond interactions have, moreover, been recognised as being of considerable importance in crystal engineering and supramolecular chemistry.[40]

Conclusion

Enantiopure nets have applications in materials science and heterogeneous catalysis and so their preparation is of intrinsic interest. We have shown that it is possible to obtain enantiopure bulk products from achiral or racemic building blocks by crystallisation-induced asymmetric transformation, as exemplified by (*R*,*R*)-**1** and (*S*,*S*)-**1**. Although enantiopure three-dimensional covalent coordination networks are formed, the topologies of the nets defined with copper(II) as

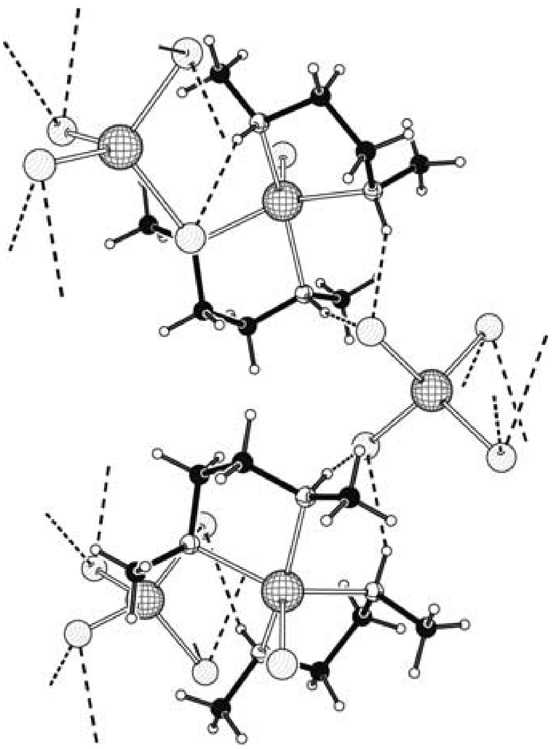

Figure 9. Part of the network formed by **3**. Broken lines indicate the short Zn-Cl···H interactions.

the nodes are not chiral. Thus, if the dmeda ligands were leached out, chirality would be lost. An additional drawback of products (*R*,*R*)-**1** and (*S*,*S*)-**1** is that the long Cu–O bond might be broken on contact with solvents and enantiomerisation could then take place.

The preparation of **2** demonstrates that it is possible to obtain an insoluble covalent chiral network from achiral or racemic building blocks. In this particular case, the compound crystallises as interpenetrating chiral nets of (10,3)-*a* topology in which the copper(I) centres form the nodes. The enantiomorphic net associated with dmeda ligands bonded to copper(II) with the (*R*,*R*) configuration exhibits helices with (*P*) configuration whereas the interpenetrating net has ligands which are solely (*S*,*S*) and helices with the (*M*) configuration. Removal of dmeda by leaching, for example, would not affect the chirality of the enantiomorphic net. Owing to the presence of the *d*-glide plane, however, an interpenetrating racemate of both enantiomorphs is formed.

On the basis of these results, we suggest total spontaneous resolution of stereochemically labile metal complexes formed from achiral or racemic building blocks as a viable route for the preparation of robust covalent chiral networks. Once the absolute structure of the compound has been determined by X-ray crystallography, a quantitative *ee* determination of the bulk product can be undertaken by means of solid-state CD spectroscopy.[2]

Experimental Section

General: Commercial methanol (>99%), *N*,*N*′-dimethylethylenediamine, $CuBr_2$, CuBr, and $Cu(NO_3)_2 \times 3H_2O$ were used without further purification. $ZnCl_2$ was dried by treatment with thionyl chloride.[41]

(*R*,*R*)-[Cu(NO$_3$)$_2$(dmeda)]$_\infty$: Copper(II) nitrate trihydrate (2.00 mmol, 0.50 g) was dissolved in methanol (20 mL), and *N*,*N*′-dimethylethylenediamine (2.00 mmol, 0.22 mL) was added. The solution was allowed to evaporate slowly, blue square pyramidal crystals of (*R*,*R*)-[Cu(NO$_3$)$_2$(dmeda)] being formed after a few days (0.48 g, 87%; *ee* >97%). UV (CH_3OH): λ_{max} = 712w, 654, 600w, 401, 303, 263 nm (values given in ref. [10]: 701, 592 nm); solid-state CD (KBr): λ = 650 (min, broad), 498 (max), 460 (min), 393 (max), 340 (min), 293 (max), 263 (min), 244 (max), 224 (min), 204 nm (max).

(*S*,*S*)-[Cu(NO$_3$)$_2$(dmeda)]$_\infty$: Crystals of (*S*,*S*)-Cu(NO$_3$)$_2$(dmeda), were prepared as for (*R*,*R*)-**1**. Yield: 0.47 g, 85%; *ee* >97%. Solid-state CD (KBr): λ = 650 (max, broad), 498 (min), 460 (max), 393 (min), 340 (max), 293 (min), 263 (max), 244 (min), 224 (max), 204 nm (min).

[{Cu^{II}Br$_2$(dmeda)}$_3$(Cu^{I}Br)$_2$]$_\infty$: Copper(II) bromide (2.00 mmol, 0.45 g) was dissolved in methanol (20 mL), and *N*,*N*′-dimethylethylenediamine (2.00 mmol, 0.22 mL) was added. The solution was allowed to evaporate slowly until small, green crystals formed. The green supernatant solution was removed and allowed to stand for several days, dark reddish brown pyramidal crystals being deposited in very low yield (<5%). Alternatively, **2** can be obtained by mixing $CuBr_2$ and CuBr under inert atmosphere. Thus, to a solution of copper(II) bromide (2.00 mmol, 0.45 g) and copper(I) bromide (1.33 mmol, 0.19 g) in dry methanol (3 mL), *N*,*N*′-dimethylethylenediamine (2.00 mmol, 0.22 mL) was added slowly, using standard Schlenk techniques. Dark reddish brown pyramidal crystals of good quality were deposited from the green solution in approximately 20% yield after a few weeks.

(*R*,*S*)-[Zn(dmeda)$_2$Cl]$_2$[ZnCl$_4$]: *N*,*N*′-dimethylethylenediamine (2.00 mmol, 0.22 mL) was added to a solution of zinc(II) chloride (2.00 mmol, 0.27 g) in methanol (4 mL). The solution was allowed to slowly evaporate slowly, colourless block-shaped crystals of **3** being formed after a few days (0.96 g, 63).

Solid-state CD spectroscopy: Solid-state CD spectra for (*R*,*R*)-**1** and (*S*,*S*)-**1** were recorded on a Jasco J-175 spectropolarimeter, using thin (100 mg) KBr disks of 13 mm diameter. For *ee* determinations, the CD signal was averaged over 15 different positions for each disk. The calibration line was obtained by preparing disks containing various amounts of enantiopure (and homochiral) crystals.[2] (In order to verify that the crystals were high-quality single crystals, they were carefully inspected under a microscope before use.) The disks were prepared by weighing a crystal sample (approximately 2 mg) and then manually mixing and grinding it with a weighed amount of KBr (approximately 1 g). The best result was obtained by adding KBr in four smaller portions, each addition being followed by careful manual grinding, until a homogeneous mixture was obtained. Approximately 100 mg of the mixture was collected and weighed before pressing it into a disk for 2 min at 8 ton. This resulted in a disk containing approximately 0.2 mg crystal mass and a similar procedure was used for all disks in Figure 2, while varying the crystal mass and/or the KBr-mediated dilution.

UV/Vis spectroscopy: UV/Vis spectra were recorded on Varian Cary 5E UV-Vis-NIR spectrometer using thin (100 mg) KBr disks for the solid-state spectra.

Crystal-structure determination: Crystal and experimental data are summarised in Table 4. Crystals of **1**–**3** were selected and mounted in glass capillaries and transferred to a Rigaku R-AXIS IIc image plate system. Diffracted intensities were measured at ambient temperature, 293(2) K, by using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) from a RU-H3R 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. Cell constants were determined by refinement based on all the reflections measured. Empirical corrections were applied for the effects of absorption using the REQAB program under CrystalClear. The structures were solved by direct meth-

Table 4. Crystallographic data for **1**–**3**.

	(*R*,*R*)-**1**	(*S*,*S*)-**1**	**2**	**3**
Formula	$C_4H_{12}CuN_4O_6$	$C_4H_{12}CuN_4O_6$	$C_{12}H_{36}Br_8Cu_5N_6$	$C_{16}H_{48}Cl_6N_8Zn_3$
M_r	275.7	275.7	1221.5	761.4
crystal system	tetragonal	tetragonal	cubic	tetragonal
T [K]	293(2)	293(2)	293(2)	293(2)
space group	$P4_12_12$	$P4_32_12$	$I\bar{4}3d$	$I\bar{4}2d$
a [Å]	8.753(2)	8.756(2)	18.201(2)	11.350(2)
b [Å]	8.753(2)	8.756(2)	18.201(2)	11.350(2)
c [Å]	12.794(3)	12.799(4)	18.201(2)	25.163(5)
V [Å^3]	980.1(3)	981.3(4)	6030(1)	3242(1)
Z	4	4	8	4
ρ_{calcd} [g cm^{-3}]	1.87	1.87	2.69	1.56
μ [mm^{-1}]	2.25	2.25	14.09	2.72
reflections meas.	7517	7416	21567	12224
no. indep. refl.	1053	1029	1082	1756
no. ($I > 2\sigma(I)$) refl.	1010	997	1081	1652
no. parameters	94	94	58	76
absolute struct. par.	0.00(2)	0.02(2)	0.01(3)	−0.01(2)
R_1	0.036	0.038	0.034	0.030
wR_2	0.088	0.082	0.061	0.058
max/min^{-1} residual [e Å^{-3}]	0.53/−0.29	0.38/−0.36	0.32/−0.38	0.24/−0.24

ods[42,43] and refined using full-matrix least-squares calculations on F^2 (SHELXL-97)[43] on all reflections, both programs operating under the WinGX program package.[44] Anisotropic thermal displacement parameters were refined for all non-hydrogen atoms and hydrogen atoms were included in **2** and **3** using a riding model. In (*R*,*R*)-**1** and (*S*,*S*)-**1**, positional and isotropic thermal parameters were refined for all the hydrogen atoms. Structural illustrations have been drawn with ORTEP-3 for Windows[45] and PLUTON[46] under WinGX.[44] Net topology drawings were made using OLEX.[47]

(*R*,*R*)-1: Blue square pyramid, $0.3 \times 0.3 \times 0.3$ mm; $2\theta_{max} = 54°$; 7517 reflections measured of which 1053 unique; 94 parameters; $R_1 = 0.036$ and $wR_2 = 0.087$ for the 1010 reflections for which $I > 2\sigma(\imath)$, $R_1 = 0.038$ and $wR_2 = 0.088$ for all 1053 reflections; Flack parameter[48] $= 0.00(2)$; maximum and minimum residual electron density: 0.53; −0.29 e Å^{-3}.

(*S*,*S*)-1: Blue square pyramid, $0.4 \times 0.4 \times 0.4$ mm; $2\theta_{max} = 54°$; 7416 reflections measured of which 1029 unique; 94 parameters; $R_1 = 0.038$ and $wR_2 = 0.082$ for the 997 reflections for which $I > 2\sigma(I)$, $R_1 = 0.039$ and $wR_2 = 0.082$ for all 1029 reflections; Flack parameter[48] $= 0.02(2)$; maximum and minimum residual electron density: 0.38; −0.36 e Å^{-3}.

Compound 2: Dark reddish brown square pyramid, $0.2 \times 0.2 \times 0.2$ mm; $2\theta_{max} = 54°$; 21567 reflections measured of which 1082 unique: 58 parameters; C2 was refined in the split positions C2a and C2b, reflecting the different ring conformations; $R_1 = 0.034$ and $wR_2 = 0.061$ for the 1081 reflections for which $I > 2\sigma(I)$, $R_1 = 0.035$ and $wR_2 = 0.061$ for all 1082 reflections; Flack parameter[48] $= 0.01(3)$; maximum and minimum residual electron density: 0.32; −0.38 e Å^{-3}.

Compound 3: Colourless block, $0.2 \times 0.2 \times 0.2$ mm; $2\theta_{max} = 54°$; 12224 reflections measured of which 1756 unique; 76 parameters; $R_1 = 0.030$ and $wR_2 = 0.056$ for the 1652 reflections for which $I > 2\sigma(I)$, $R_1 = 0.035$ and $wR_2 = 0.058$ for all 1756 reflections; Flack parameter[48] $= -0.01(2)$; maximum and minimum residual electron density: 0.24; −0.241 e Å^{-3}.

CCDC-261074 [(*R*,*R*)-**1**], -261075 [(*S*,*S*)-**1**], -261076 (**2**) and -261077 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/

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