

First structurally authenticated inorganic polymers of CuBr and CuI containing chiral bidentate *N*-donor ligands. Use of the Schiff base 2,2'-bis[(4*S*)-4-benzyl-2-oxazoline] as ligand

David M. Haddleton,* David J. Duncalf, Andrew J. Clark, Martin C. Crossman and Dax Kukulj

Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL

The products from the reaction of CuBr and CuI with equimolar quantities of 2,2'-bis[(4*S*)-4-benzyl-2-oxazoline] have been characterised by X-ray crystallography and shown to comprise two different polymeric arrangements of (CuBr)_n or (CuI)_n 'sheathed' by bridging bidentate oxazoline ligands.

Inorganic polymers of the transition metals have aroused much interest as new materials for use in electronic, magnetic and optical applications.¹ Recently, several examples of polymeric copper(I) complexes, particularly Schiff base adducts, have appeared in the literature.² Our interest in copper(I) Schiff base complexes arises from their use as highly effective atom transfer polymerisation catalysts for the polymerisation of vinyl monomers such as methyl methacrylate³ and styrene.⁴ We have shown that the catalysts formed from the reaction of CuX (X = Br or BF₄), with suitable bidentate Schiff bases, led to discrete molecules of formula [Cu(L)₂][X]⁵ and indeed other similar structures have been characterised.⁶

As part of our investigations directed toward the development of further copper(I) based atom-transfer polymerisation catalysts containing an enantiomerically pure chiral centre designed for a potential route to stereo-controlled polymerisation of vinyl monomers, we investigated the complex formed by the reaction between CuX (X = Br or I) and the enantiomerically pure Schiff base 2,2'-bis[(4*S*)-4-benzyl-2-oxazoline] (L¹). Attempted polymerisation of methyl methacrylate using copper(I) salts and L¹ invariably result in the formation of a brightly coloured precipitate and no formation of polymer; however, the reaction of CuBr and CuI with L¹ produced crystals suitable for X-ray analysis. The crystal structures, surprisingly, showed that rather than preparing the expected product (containing discrete [CuL₂][X] units), the structure comprised CuBrL¹ and Cu₂I₂L¹ repeat units arranged in a polymeric fashion. The bidentate oxazoline ligands bridge adjacent copper centres and these compounds are the first inorganic polymers of (CuBr) or (CuI) containing chiral bidentate ligands. Interestingly, the two structures are somewhat different to each other.

In the CuBr derived polymer† (Fig. 1), [CuBrL¹], the

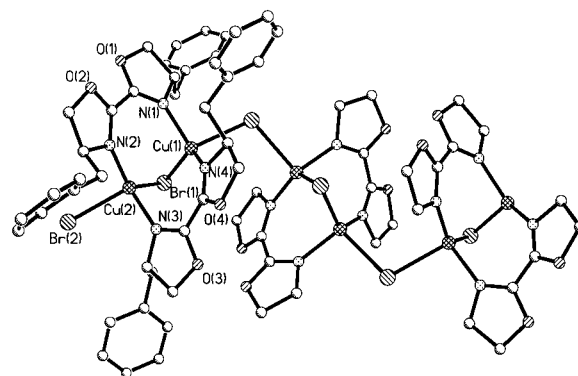
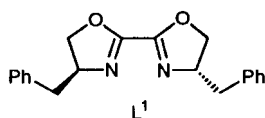


Fig. 1 Structure of the [CuBrL¹] polymer showing three repeat units (for clarity only the benzyl rings on the bis-oxazoline ligands on the first repeat unit are shown)

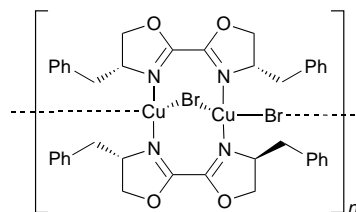


Fig. 2 Repeat unit for [CuBrL¹]

overall arrangement of copper and bromine atoms may be described as that of a chain composed of a single zigzag strand of alternating Cu(1)—Br(1)—Cu(2)—Br(2) units, where the two copper atoms are doubly bridged by two oxazoline ligands, and the ligands themselves form a helical screw along the length of the chain (Fig. 2). This arrangement results in each copper being co-ordinated by two nitrogen and two bromine atoms in a pseudo-tetrahedral arrangement. The Cu(1)—Br(1) bond length of 2.4853(12) Å is essentially equivalent to the Br(1)—Cu(2) length of 2.484(2) Å; however, the

* Fax: +44 (0) 1203 524112; E-mail: msrgs@csv.warwick.ac.uk

† Crystal data for [CuBrL¹](CH₃)₂O: C₄₃H₄₆Br₂Cu₂N₄O₅: *M* = 985.74, monoclinic, space group *C*2, *a* = 25.4558(4), *b* = 12.3569(2), *c* = 18.2232(2) Å, β = 134.28(3)°, *U* = 4103.74(10) Å³, *Z* = 4, *D*_c = 1.595 Mg m⁻³, Mo-Kα (λ = 0.710 73 Å), *T* = 180 K, μ = 3.034 mm⁻¹, crystal size 0.3 × 0.2 × 0.2 mm, max. 2θ = 48.00°. 9973 Reflections were collected; 6264 independent with 6027 observed [*I* > 2σ(*I*)]. Final *R* = 0.0507 (6027 reflections) and *wR*2 = 0.1387 (all data). Max./min. residual electron density = 1.071 and -1.553 e Å⁻³. Absolute structure parameter (Flack parameter) -0.030(13).

‡ Crystal data for [Cu₂I₂L¹]: C₂₀H₂₀Cu₂I₂N₂O₂: *M* = 701.26, orthorhombic, *P*2₁2₁2, *a* = 19.9240(10), *b* = 8.5321(10), *c* = 12.6340(10) Å, *U* = 2147.70(3) Å³, *Z* = 4, *D*_c = 2.169 Mg m⁻³, Mo-Kα (λ = 0.710 73 Å), *T* = 180 K, μ = 4.873 mm⁻¹, crystal size 0.3 × 0.1 × 0.1 mm, max. 2θ = 57.25°. 13 633 Reflections were collected; 5057 independent with 4808 considered observed [*I* > 2σ(*I*)]. Final *R* = 0.0296 (4808 reflections) and *wR*2 = 0.0736 (all data). Max./min. residual electron density = 0.967 and -0.909 e Å⁻³. Absolute structure parameter (Flack parameter) 0.02(3).

Cu(2)—Br(2) bond length of 2.6595(10) Å is longer. The Cu(1)—Cu(2) distance, 2.7918(11) Å, is relatively short and is approaching the distance found in metallic copper, 2.56 Å.⁷ The copper–nitrogen distances: Cu(1)—N(1) 2.035(6), Cu(1)—N(4) 1.997(6), Cu(2)—N(2) 1.996(6) and Cu(2)—N(3) 2.048(6) Å compare well to other Cu—N bond lengths in similar compounds.⁵

The CuI derived polymer[‡] (Fig. 3), [Cu₂I₂L¹], has a different structure to [CuBrL¹]. Two repeat units are shown in Fig. 4 with only the nitrogens of the bis-oxazoline ligands drawn for clarity. In this case, the chain is best described as a ribbon or stair with each tetrahedrally ligated copper co-ordinated by three iodine and only one nitrogen atom. This arrangement of (CuI) has been reported previously in connection with polymers formed from the reaction of CuI and pyridine-type ligands.⁸ The Cu(1)—I(1) bond length is 2.5738(8) Å and Cu(2)—I(1) [2.6889(7) Å] is longer. The Cu(2)—I(2) bond length of 2.6749(7) Å is slightly shorter than Cu(2)—I(1). The Cu(1)—N(2), 2.035(4) Å, and Cu(2)—N(1) [2.048(4) Å] bond lengths are also consistent with other reported values,⁶ and Cu(1)—Cu(2) [2.8429(9) Å] is slightly longer than that found in the CuBr derived polymer (see above). It is interesting that in contrast to the CuBr-derived polymer, where an alternating chain of (CuBr) is observed, in this case, the copper and iodine arrangement results in an unbroken strand of copper atoms running through the length of the chain. It is envisaged that such characteristics may give rise to interesting and useful electronic and magnetic properties. Also, as observed for the CuBr polymer, the bis-oxazoline ligands form a helical screw thread around the CuI chain.

The crystal structure of [CuBrL¹], Fig. 5, shows ring-stacking interactions; each CuBr chain interacts with neighbouring chains *via* the benzyl substituents. The structure of [Cu₂I₂L¹] does not show such pronounced interactions, Fig. 6; however, the orientation of the benzyl ring substituents which ‘face’ other benzyl rings on neighbouring chains does suggest interchain interactions. Unfortunately this ligand is ineffective in promoting atom-transfer polymerisation due to the insolubility of the inorganic polymers in the reaction media.

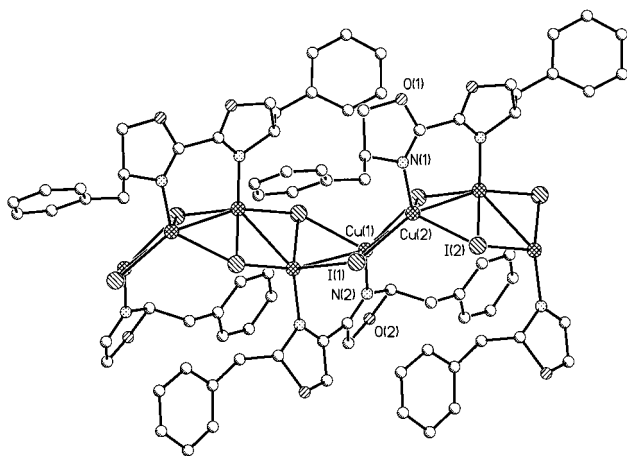


Fig. 3 Structure of the [Cu₂I₂L¹] polymer showing four repeat units

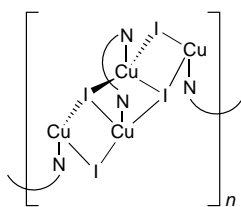


Fig. 4 Two repeat units for [Cu₂I₂L¹] (for clarity only the nitrogen atoms of the bis-oxazoline ligands are shown)

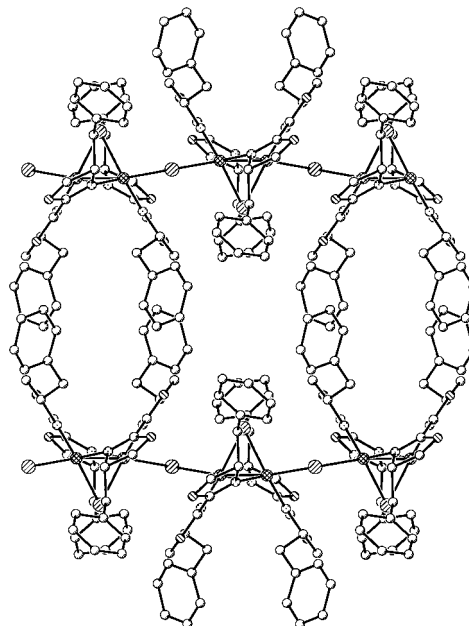


Fig. 5 View along the *a* axis of [CuBrL¹] showing the ring stacking interactions

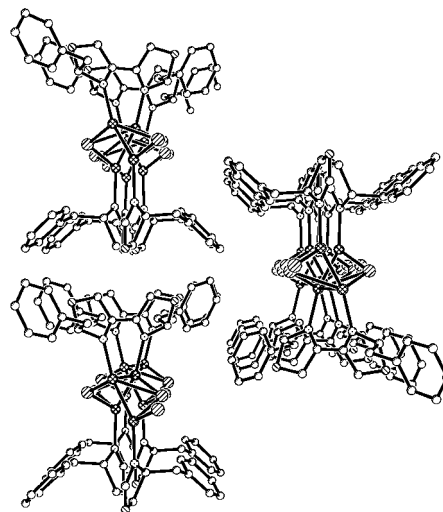


Fig. 6 A portion of the crystal packing diagram for [Cu₂I₂L¹], viewed along the *b* axis

Experimental

All manipulations were performed using standard Schlenk line or syringe techniques under an atmosphere of nitrogen. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wyckoff,⁹ copper(I) iodide (Aldrich, 99.999%) and (*S,S*)-4,4'-dibenzyl-2,2'-bis(2-oxazoline) (Fluka, 98%) were used as received. The inorganic polymers were prepared by the addition of CuBr (0.1 g, 6.97 × 10^{−4} mol) or CuI (0.13 g, 6.83 × 10^{−4} mol) to L¹ (0.22 g, 6.91 × 10^{−4} mol) under nitrogen in anhydrous acetonitrile solvent (5 ml). After stirring overnight, the solutions were filtered and cooled to −20 °C yielding orange crystals. The specific optical rotation, [α]_D²⁹⁸, for [CuBrL¹] is −142.0° and for [Cu₂I₂L¹] is −84.5°. Satisfactory analyses for both compounds were obtained. The data collection was performed on a Siemens SMART system equipped with CCD area collector. The structures were solved by direct methods using SHELXTL^{10a} version 5 software and the refinements were carried out using SHELXTL96^{10b} software, minimising on the weighted *R* factor *wR*₂. Anisotropic thermal parameters were used for all non-H atoms whilst

hydrogen atoms were inserted at calculated positions and fixed, with isotropic thermal parameters ($U = 0.08 \text{ \AA}^3$), riding on the supporting atom.

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