Letter

Chiral heterocyclic ligands. Part 9. Homoconfigurational coordination polymers based on a C_2-symmetric, linear-bridging ligand†

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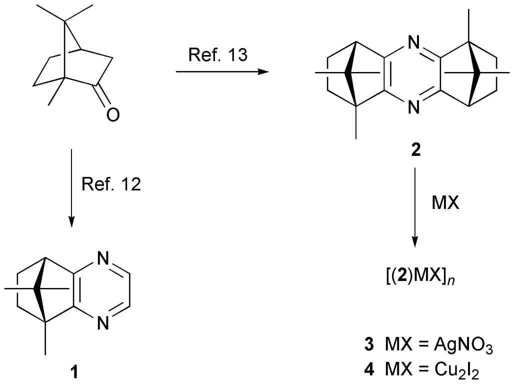
The fusion of two bornane units to a pyrazine ring gives a sterically hindered C_2-symmetric linear bridging ligand that readily assembles into one-dimensional coordination polymers; X-ray crystal structures are described for the free ligand and metallopolymers formed by reaction with silver(I) nitrate and copper(I) iodide.

The use of linear bridging heterocyclic ligands,[1] such as pyrazine and 4,4′-bipyridine, for the assembly of one-dimensional coordination polymers has been the subject of intense recent study.[2] The controlled synthesis of chiral coordination compounds is also an area of much current interest,[3] to which there are two common approaches. One method is to use the intrinsic stereochemistry of transition metal centres to control the chirality of the resultant coordination compounds.[4] Alternatively, the use of enantiopure ligands, derived from natural products, allows facile control of the chiral structure of metal complexes.[5] Monoterpenes have proved to be a particularly useful subclass of the chiral pool for incorporation, *via* simple synthetic procedures, into various types of ligands for coordination to metal centres.[6] For example, von Zelewsky and coworkers[7] have prepared chiral transition metal complexes using a diverse array of chelating and bridging ligands containing pinene subunits. We,[8] and others,[9] have previously reported the synthesis, and applications in asymmetric catalysis, of various chiral ligands that contain a bornane subunit fused to a pyrazole ring. Other workers have described ligands with bornane units fused to pyridine rings[10] and other heterocycles.[11] We now report the first use of a C_2-symmetric ligand, which contains a central pyrazine ring fused to two bornane groups, for the preparation of homoconfigurational one-dimensional coordination polymers.

Our initial work in this area centred on the readily available[12] C_1-symmetric ligand **1**. However, this line of investigation proved unfruitful for the controlled assembly of ordered coordination polymers, due to the inability of this ligand to faithfully assemble in a single orientation, because of the similar, but subtly different, nature of the two nitrogen donors. To avoid this problem, we decided to use the C_2-symmetric ligand **2**, which has two identical donors. This compound was first prepared almost ninety years ago,[13] but, curiously, its coordination chemistry has not been explored previously. It is readily prepared[13,14] from natural camphor in three steps by oxidative dimerisation of 3-aminocamphor, which we carried out using ferric chloride as the oxidant (Scheme 1). In order to confirm the structure of the ligand and to examine the steric environment of the nitrogen donors, an X-ray structure of **2** was determined. This compound‡ crystallizes about a crystallographic 2-fold rotation axis in the orthorhombic space group $P2_12_12$ with half a molecule in the asymmetric unit (Fig. 1). Space filling representations of the structure show a relatively hindered environment for the potential nitrogen donors of the planar central pyrazine ring. Because of this steric encumbrance,[15] we felt that this ligand would be ideally suited for the controlled formation of one-dimensional coordination polymers.

Since silver(I) salts readily form coordination polymers with bridging ligands,[16] such as pyrazine[17] and 4,4′-bipyridine,[18] we first examined the reaction of **2** with silver nitrate. This produced a compound **3**§ in modest yield, the structure of which was determined by single crystal X-ray crystallography.‡ Compound **3** crystallizes in the orthorhombic space group $P2_12_12$, with the asymmetric unit comprising two independent silver atoms, two molecules of **2**, two nitrate counterions and three solvate molecules. Fig. 2 shows a perspective view of a section of this one-dimensional metallopolymer, which propagates along a crystallographic two-fold screw axis. The nitrate counterions and the solvate molecules occupy the sites between the polymer chains. The nitrate oxygen atoms experience weak interactions (>2.6 Å) with the silver atoms.



Scheme 1

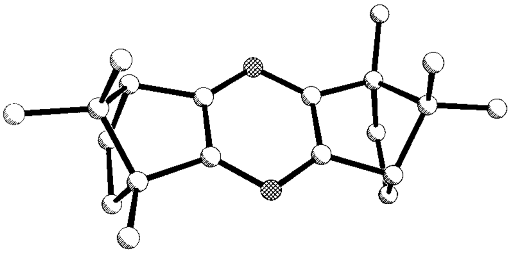


Fig. 1 Perspective view of the crystal structure of **2**. Hydrogen atoms are not shown.

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† For part 8, see: ref 8.

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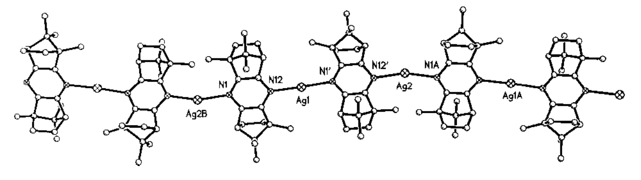

Fig. 2 Perspective view of a section of the major contributor to the crystal structure of the metallopolymer **3**. Hydrogen atoms, the nitrate counterions and the methanol and water solvate molecules are not shown. Selected bond lengths (Å) and angles (°): Ag1–N1′ 2.187(3); Ag1–N12 2.191(3); Ag2–N1A 2.256(5); Ag2–N12′ 2.260(5); N1A–Ag1–N12 173.80(14); N1A–Ag2–N12A 156.9(2).

Within the complex **3**, the two independent molecules of **2** have similar bonding geometry and each has internal, albeit non-crystallographic, C_2 symmetry. Of the two independent silver atoms, Ag1 has linear two-coordinate geometry and bridges two molecules of **2** that have their mean planes inclined at an angle of 49.9(1)°; these two ligands are aligned in a head-to-tail fashion. In contrast, Ag2 bridges two ligands that have their mean planes inclined at an angle of 129.1(1)°, and are arranged in a head-to-head manner. This silver atom displays some positional disorder[‡] (not shown in Fig. 2) and shows a greater deviation from linearity, which we believe to be due to the slightly closer proximity of a nitrate oxygen [Ag2–O11 = 2.636(2) Å] compared to that the other silver [Ag1–O21 = 2.727(2) Å]. The two-coordinate geometry of the silver atoms reflects the sterically demanding nature of this bridging ligand, which is also manifested in the relatively long silver–nitrogen bond lengths. The two independent molecules of **2** separate their coordinated silver atoms by 7.292(4) and 7.313(4) Å, which is somewhat longer than in the complex with the parent heterocyclic pyrazine.[1,17]

We next explored the reaction of **2** with copper(I) iodide, which also readily forms coordination polymers.[16a] Reaction of **2** with 1 equiv. of cuprous iodide produced a product **4**[¶] in good yield, whose elemental analysis revealed to have an intriguing 4 : 3 metal : ligand composition. The X-ray crystal structure[‡] of this compound was also determined (Fig. 3). This complex crystallizes in the monoclinic space group $C2$ and consists of chains of Cu_2I_2 units bridged by molecules of **2**. The space between the chains is occupied by non-coordinated molecules of **2**, which make no significantly close contacts with the polymer chains. The asymmetric unit contains two independent Cu_2I_2 units (each showing minor positional disorder), two coordinated molecules of **2** and two non-coordinated half molecules of **2**, each lying on crystallographic two-fold rotation axes.

The one-dimensional polymeric structure with CuI_2Cu bridges is similar to that reported for the cuprous iodide complex of the structurally similar, but achiral, ligand phenazine.[19] The formation of a Cu_2I_2 based coordination polymer, in preference to other more complex CuI species, again reflects the high steric demand of the bridging ligand.[20] This is also reflected in an elongation of the Cu–N bonds, compared to the corresponding complex with phenazine.[19] The polymer chain propagates along the c axis, with the ligands bridging Cu_2I_2 units separated by 6.898(3) and 6.908(3) Å, for the two independent ligands, respectively. The planes of the two independent central pyrazine rings are rotated by an angle of 15.5(1)°. The Cu_2I_2 units are non-planar with the iodine atoms displaced away from the plane to minimize steric interactions with nearby methyl groups. The copper atoms have trigonal coordination and the geometries of the Cu_2I_2 units differ slightly (Fig. 3). One of the units has a particularly short Cu···Cu contact [2.514(1) Å].[20,21]

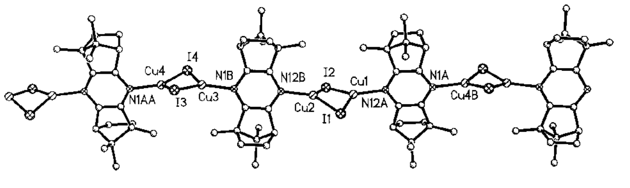

Fig. 3 Perspective view of a section of the metallopolymer **4**. Hydrogen atoms and the non-coordinated molecules of **2** are not shown. Only the major (*ca.* 88%) contributors of the Cu_2I_2 units are shown. Selected bond lengths (Å) and angles (°): Cu1–N12A 2.021(4); Cu1–I2 2.5548(13); Cu1···Cu2 2.5790(16); Cu1–I1 2.6012(14); I1–Cu2 2.5539(14); Cu2–N12B 2.013(5); Cu2–I2 2.6549(16); Cu3–N1B 2.003(4); Cu3–Cu4 2.510(3); Cu3–I3 2.5796(11); Cu3–I4 2.587(4); I3–Cu4 2.605(3); Cu4–N1AA 2.002(5); Cu4–I4 2.572(3); N12A–Cu1–I2 131.28(16); N12A–Cu1–I1 109.92(16); I2–Cu1–I1 118.56(4); Cu2–I1–Cu1 60.03(4); N12B–Cu2–I1 126.58(15); N12B–Cu2–I2 115.72(14); I1–Cu2–I2 116.63(6); Cu1–I2–Cu2 59.31(4); N1B–Cu3–I3 121.13(13); N1B–Cu3–I4 118.18(16); I3–Cu3–I4 120.37(10); Cu3–I3–Cu4 57.91(7); N1AA–Cu4–I3 118.8(2); I4–Cu4–I3 119.99(15); Cu4–I4–Cu3 58.22(9).

In conclusion, we have shown that the enantiopure C_2-symmetric ligand **2** is a useful linear bridging ligand for the formation of chiral one-dimensional coordination polymers.

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Notes and references

[‡] *Crystal data* for **2**: $C_{20}H_{28}N_2$, $M = 296.44$, orthorhombic, $P2_12_12$; $a = 10.752(6)$, $b = 11.359(6)$, $c = 7.382(4)$ Å, $U = 901.6(8)$ Å^3, $Z = 2$, $T = -103$ °C, $\mu = 0.064$ mm^{-1}, 10 913 reflections collected, 1835 unique (98.6% completeness), 1485 with $F^2 > 2\sigma(F^2)$. Final $R = 0.044$ (obsd), $wR(F^2) = 0.115$ (all).

For **3**: $[Ag_2(\mathbf{2})_2 \cdot (NO_3)_2 \cdot 1.5MeOH \cdot H_2O]_n$, $M = 998.7$, orthorhombic, $P2_12_12$; $a = 13.614(5)$, $b = 28.871(10)$, $c = 11.523(5)$ Å, $U = 4529(3)$ Å^3, $Z = 4$, $T = -110$ °C, $\mu = 0.921$ mm^{-1}, 59 156 reflections collected, 9250 unique (99.7% completeness), 6208 with $F^2 > 2\sigma(F^2)$. Final $R = 0.036$ (obsd), $wR(F^2) = 0.077$ (all).

For **4**: $[Cu_4I_4(\mathbf{2})_3]_n$, $M = 1651.1$, monoclinic, $C2$; $a = 23.808(9)$, $b = 14.984(6)$, $c = 18.715(7)$ Å, $U = 6658(5)$ Å^3, $Z = 4$, $T = -110$ °C, $\mu = 3.154$ mm^{-1}, 37 544 reflections collected, 13 247 unique (98.3% completeness), 12 549 with $F^2 > 2\sigma(F^2)$. Final $R = 0.041$ (obsd), $wR(F^2) = 0.106$ (all).

CCDC reference number 440/231. See http://www.rsc.org/suppdata/nj/b0/b005881p/ for crystallographic files in .cif format.

All data were collected using a Bruker SMART CDD diffractometer with Mo-Kα radiation ($\lambda = 0.710 73$ Å). Structure solutions and refinements were carried out with SHELX-97. In the structure of **3**, the position of one of the silver atoms (Ag2) is disordered over two sites with a 3 : 1 ratio of occupancies. One of the nitrate counterions is disordered over two sites, each of which lies on a two-fold rotation axis. The half-occupancy methanol solvate molecule is disordered about a crystallographic two-fold rotation axis. In the structure of **4**, there is minor disorder of each of the Cu_2I_2 units, with the major contributor representing *ca.* 88% in each case. The absolute configurations of **3** and **4** were determined by the Flack parameter and are consistent with the known absolute configuration of the starting camphor. That of **2** was assigned to be the same.

[§] *Preparation of* **3**: Reaction of **2** (14.9 mg, 0.05 mmol), dissolved in hot acetone, with silver nitrate (17.4 mg, 0.10 mmol), dissolved in hot methanol, gave a colourless solution. Crystals suitable for single crystal X-ray structure determination were obtained on cooling the solution to 4 °C for 7 days. An analytically pure sample was obtained by addition of ether to the solution. Yield 7.5 mg (31%). Mp > 265 °C (dec.). Anal. found: C, 50.16; H, 5.99; N, 8.55. Calc. for $C_{40}H_{56}N_6O_6Ag_2 \cdot MeOH \cdot H_2O$: C, 50.11; H, 6.36; N, 8.55%.

[¶] *Preparation of* **4**. Reaction of **2** (14.7 mg, 0.05 mmol), in hot acetonitrile, with copper iodide (9.8 mg, 0.051 mmol), in hot acetonitrile, gave a yellow solution. Yellow crystals suitable for single crystal X-ray structure determination were obtained from the slow evaporation this solution. Yield 15.7 mg (76%). Mp > 310 °C (dec.). Anal. found: C, 43.57; H, 4.84; N, 5.20. Calc. for $C_{30}H_{42}N_3Cu_2I_2$: C, 43.65; H, 5.13; N, 5.09%.

1 P. J. Steel, *Coord. Chem. Rev.*, 1990, **106**, 227.
2 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638, and references therein.
3 C. Provent and A. F. Williams, in *Transition Metals in Supramolecular Chemistry*, ed. J.-P. Sauvage, Wiley, Chichester, 1999, ch. 4, p. 135; A. von Zelewsky, *Stereochemistry of Coordination Compounds*, J. Wiley, Chichester, 1996.

4 F. Barigelletti and L. Flamigni, *Chem. Soc. Rev.*, 2000, **29**, 1; U. Knof and A. von Zelewsky, *Angew. Chem., Int. Ed.*, 1999, **38**, 303; J. B. Chen and F. M. MacDonnell, *Chem. Commun.*, 1999, 2529; F. R. Keene, *Chem. Soc. Rev.*, 1998, **27**, 185; M. Ziegler and A. von Zelewsky, *Coord. Chem. Rev.*, 1998, **177**, 257.

5 A. Pfaltz, *J. Heterocycl. Chem.*, 1999, **36**, 1437.

6 H.-U. Blaser, *Chem. Rev.*, 1992, **92**, 935; W. Oppolzer, *Tetrahedron*, 1987, **43**, 1969.

7 A. von Zelewsky and O. Mamula, *J. Chem. Soc., Dalton Trans.*, 2000, 219, and references therein.

8 (*a*) A. A. Watson, D. A. House and P. J. Steel, *Aust. J. Chem.*, 1995, **48**, 1549; (*b*) A. A. Watson, D. A. House and P. J. Steel, *J. Org. Chem.*, 1991, **56**, 4072, and references therein.

9 B. Therrien, A. Koenig and T. R. Ward, *Organometallics*, 1999, **18**, 1565; W.-H. Fung, W.-Y. Yu and C.-M. Che, *J. Org. Chem.*, 1998, **63**, 7715; M. Barz, H. Glas and W. Thiel, *Synthesis*, 1998, 1269; M. C. Lopez, N. Jagerovicz and P. Ballesteros, *Tetrahedron:Asymmetry*, 1994, **5**, 1887; D. D. LeCloux, C. J. Tokar, M. Osawa, R. P. Houser, M. C. Keyes and W. B. Tolman, *Organometallics*, 1994, **13**, 2855; H. Brunner, U. P. Singh, T. Boeck, S. Altmann, T. Scheck and B. Wrackmeyer, *J. Organomet. Chem.*, 1993, **443**, C16; H. Brunner and T. Scheck, *Chem. Ber.*, 1992, **125**, 701; C. J. Tokar, P. B. Kettler and W. B. Tolman, *Organometallics*, 1992, **11**, 2737.

10 C. Chen, K. Tagami and Y. Kishi, *J. Org. Chem.*, 1995, **60**, 5387; G. Chelucci, S. Gladiali and M. Marchetti, *J. Heterocycl. Chem.*, 1988, **25**, 1761; G. Chelucci, G. Delogu, S. Gladiali and F. Soccolini, *J. Heterocycl. Chem.*, 1986, **23**, 1395; C. Botteghi, A. Schionato, G. Chelucci, H. Brunner, A. Kuerzinger and U. Obermann, *J. Organomet. Chem.*, 1989, **370**, 17.

11 G. Chelucci and R. P. Thummel, *Synth. Commun.*, 1999, **29**, 1665; S.-I. Nagai, T. Ueda, M. Takamura, A. Nagatsu, N. Murakami and J. Sakakibara, *J. Heterocycl. Chem.*, 1998, **35**, 293; S.-I. Nagai, T. Ueda, A. Nagatsu, K. Nakaoka, N. Murakami, J. Sakakibara, M. Fujita and Y. Hotta, *J. Heterocycl. Chem.*, 1998, **35**, 329; N. Sewald and Y. Wendisch, *Tetrahedron: Asymmetry*, 1996, **7**, 1269; I. Ito, N. Oda, S.-I. Nagai and Y. Kudo, *Heterocycles*, 1977, **8**, 319.

12 J. Elguero and B. Shimizu, *An. Quim., Ser. C*, 1988, **84**, 196.

13 M. O. Forster and H. Spinner, *J. Chem. Soc.*, 1912, **101**, 1340.

14 T. Kobayashi, S. Yamamoto and H. Kato, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 1193; H. E. Smith and A. A. Hicks, *J. Org. Chem.*, 1971, **36**, 3659; R. C. Cookson, J. Hudec, A. Szabo and G. E. Usher, *Tetrahedron*, 1968, **24**, 4353.

15 H. Kotsuki, H. Sakai, J.-G. Jun and M. Shiro, *Heterocycles*, 2000, **52**, 661.

16 (*a*) M. Munakata, L. P. Wu and T. Kuroda–Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173, and references therein; (*b*) D. A. McMorran and P. J. Steel, *Inorg. Chem. Commun.*, 1999, **2**, 368; (*c*) C. Richardson and P. J. Steel, *Inorg. Chem. Commun.*, 1998, **1**, 260; (*d*) C. M. Hartshorn and P. J. Steel, *J. Chem. Soc., Dalton Trans.*, 1998, 3927; (*e*) C. M. Hartshorn and P. J. Steel, *J. Chem. Soc., Dalton Trans.*, 1998, 3935.

17 D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Inorg. Chem.*, 1995, **34**, 5698; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562.

18 A. J. Blake, N. R. Champness, M. Crew and S. Parsons, *New J. Chem.*, 1999, **23**, 13; O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295; F. Robinson and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1995, 2413; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1994, 2755.

19 M. Munakata, T. Kuroda–Sowa, M. Maekawa, A. Honda and S. Kitagawa, *J. Chem. Soc., Dalton Trans.*, 1994, 2771.

20 L. R. Hanton and K. Lee, *J. Chem. Soc., Dalton Trans.*, 2000, 1161; A. J. Blake, N. R. Brooks, N. R. Champness, P. A. Cooke, A. M. Deveson, D. Fenske, P. Hubberstey, W.-S. Li and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1999, 2103.

21 S. Jagner and G. Helgesson, *Adv. Inorg. Chem.*, 1991, **37**, 1.