ChemComm

Design, synthesis and structural investigation of a 1-D directional coordination network based on the self-assembly of an unsymmetrical mono-tridentate ligand and cobalt cation

Abdelaziz Jouaiti, Mir Wais Hosseini* and André De Cian

Laboratoire de Chimie de Coordination Organique, Université Louis Pasteur, F-67000 Strasbourg, France, UMR CNRS 7513

Received (in Cambridge, UK) 27th July 2000, Accepted 24th August 2000
First published as an Advance Article on the web

Using an *exo* ligand containing a pyridine unit as a monodentate coordination site and a PyS_2 moiety as a tridentate coordination pole, a directional 1-D coordination network has been obtained in the presence of $CoCl_2$ under self-assembly conditions; a single-crystal X-ray study revealed that in the crystalline phase the 1-D networks are packed in a centrosymmetric fashion.

The formation of coordination networks based on *exo* ligands (ligands with coordination sites outwardly oriented) and metal cations are currently attracting much attention.[1] The formation of such networks may take place in the crystalline phase through self-assembly processes based on the reversible coordination of metal cations by *exo* ligands. The iterative binding process leads to the assembling cores acting as structural nodes of the network. The dimensionality of coordination networks (1-, 2- or 3-D) is defined by the number of translations (1, 2 or 3) operating on the assembling core. The dimensionality depends, on one hand, on the topological and coordination features of the organic *exo* ligand and, on the other hand, on the stereochemical requirements of the metal. Although the majority of reported coordination networks are formed using bis-monodentate *exo* ligands based on 4,4′-bipyridine,[2] examples of coordination networks based on bis-bidentate[3,4] or tetrakis-monodentate[5,6] ligands have also been reported. However, dealing with bis-tridentate *exo* ligands, only a few structurally characterised networks have been published.[7–9]

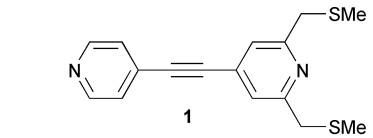
At present, let us consider the formation of 1-D coordination networks based on a single translation of an assembling core. For such a network, owing to the fact that exploitation of directional physical properties requires vectorial arrangements of the building blocks, the control of directionality remains a challenging issue.

The design of ligands for the formation of 1-D networks using metals with linear coordination geometry is trivial and may only be based on bis-monodentate systems (one may use homo-L(*n*,*m*) and hetero-L(*n*,*m*) notation to design the *exo* ligand L composed of two coordination poles each containing *n* and *m* coordination sites of the same (homo) or different (hetero) nature: thus, bis-monodentate ligands may be described as homo- or hetero-L(1,1) and bis-bidentate ligands as homo- or hetero-L(2,2) *etc*.). For metal cations requiring four coordination sites arranged either in square planar or in tetrahedral coordination geometry, two different types of *exo* ligands based on either bis-bidentate (homo- or hetero-L(2,2)) or a combination of mono ($n = 1$) and tridentate ($m = 3$) (hetero-L(1,3) may be envisaged. For metal cations with octahedral coordination geometry, if all six coordination positions are taken into account, 1-D networks may be obtained using bis-tridentate *exo* ligands (homo- or hetero-L(3,3)). However, in the latter case, further design of the assembling core may be based on the use of four coordination positions located at the square planar base of the octahedron. In such a design the two axial positions would be occupied by two ligands acting as terminal coordinators and thus not participating in the formation of the network. Again, for such a strategy, one may use either homo- or hetero-L(2,2) or hetero-L(1,3) ligands. Whereas for symmetrical ligands of the homo-L(2,2) type no directional network may be formed, with hetero-L(2,2) or hetero-L(1,3) ligands the formation of directional 1-D networks may be envisaged.

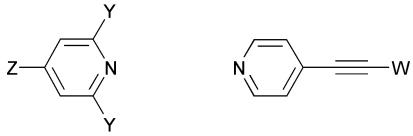
In the present contribution we report the design and synthesis of a new hetero-L(1,3) *exo* ligand **1** and its self assembly in the crystalline phase into a 1-D directional network in the presence of $CoCl_2$.

The strategy that was followed for the design of 1-D directional networks was based on the self-assembly of the neutral hetero-L(1,3) *exo* ligand **1** and octahedral $CoCl_2$ complex. The design of **1** (Scheme 1) is based on a combination of two different coordination poles, one composed of a monodentate pyridine derivative and the other on a pyridine unit bearing at the 2 and 6 positions CH_2SCH_3 thioether fragments leading thus to a tridentate PyS_2 coordination system. The ethynyl spacer was chosen to interconnect the two coordination poles through the pyridine units at the 4 positions. The ethynyl spacer appeared as an interesting bridge since it should allow avoidance of possible steric effects which may alter the packing of 1-D networks in the solid state and based on its ability to permit possible electronic communication between the two pyridine rings.

The starting material for the synthesis of **1** was chelidamic acid **2**. Upon treatment of the latter with PBr_5 followed by EtOH, compound **3** was obtained in 61% yield.[10] The latter was reduced to **4** in 62% yield using $NaBH_4$ in dry EtOH.[11] Although the preparation of compound **5** from the diol **4** was reported using PBr_3,[11] it was found that bromination of **4** using 33% HBr/AcOH at 125 °C for 5 h was much more efficient and produced compound **5** in 89% yield. Treatment for 48 h at r.t. of **5** by NaSMe (2 eq.) in dry THF afforded **6** in 60% yield. The synthesis of the ligand **1** was achieved by coupling the bromopyridine derivative **6** with 4-ethynylpyridine **7** in the presence of $Pd(OAc)_2$ and Ph_3P in Et_3N under reflux for 48 h. The pure compound **1** was obtained in 94% yield as a colourless viscous oil after chromatography (SiO_2, CH_2Cl_2/MeOH 0–1%).



1



2 Y = CO_2H, Z = OH
3 Y = CO_2Et, Z = Br
4 Y = CH_2OH, Z = Br
5 Y = CH_2Br, Z = Br
6 Y = CH_2SMe, Z = Br

7 W = H
8 W = $C(CH_3)_2OH$

Scheme 1

DOI: 10.1039/b006099m

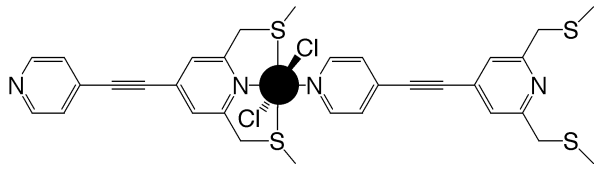


Fig. 1 Representation of the assembling core based on the coordination of $CoCl_2$ complex by two consecutive ligands **1** which by translation leads to the directional 1-D network.

Compound **7** was obtained in two steps upon treatment at r.t. of 4-bromopyridine hydrochloride by 2-methyl-3-butyn-2-ol in the presence of $(PPh_3)_2PdCl_2$ and CuI in diethylamine affording compound **8** and the removal of the protecting group by treatment under reflux with NaOH in toluene.[12]

Upon slow diffusion at r.t. of a MeOH solution containing $CoCl_2{\cdot}6H_2O$ (8 mg, 6.1 mmol) into a CH_2Cl_2 solution of compound **1** (8 mg, 3.3 mmol), purple crystals were obtained after three weeks. A single-crystal X-ray study† showed the following relevant features: the crystal (orthorhombic) was composed of **1**, $CoCl_2$ and MeOH molecules. As expected, a directional 1-D neutral network based on the interconnection of $CoCl_2$ units by the ligand **1** is observed. The assembling core is a distorted octahedral Co(II) complex for which the coordination sphere is composed of two Cl^- anions, two nitrogen and two sulfur atoms. The two Cl^- anions are located at axial positions with a Co–Cl distance of 2.425 Å and a Cl–Co–Cl angle of 178.8°. The square base of the octahedron is composed of one pyridine and one NS_2 coordination set belonging to the tridentate moiety of the ligand with Co–N and Co–S distances of 2.118 Å and 2.490 Å respectively. Whereas the ClCoS angle varies from 85° to 95°, the ClCoN angle is *ca.* 90° and the NCoN angle is 180.0°. Dealing with the ligand **1**, the two pyridine units are almost untilted and the CC triple bond distance is 1.207 Å (Fig. 1).

Owing to the unsymmetrical nature of the ligand **1** and, thus, the assembling core, upon a single translation a 1-D directional coordination network is indeed obtained. In the crystalline phase, in principle, a directional 1-D network may either be packed in centrosymmetric (Fig. 2a) or non-centrosymmetric modes (Fig. 2b). In the case reported here, the directional networks are positioned in a parallel fashion but oriented in opposite directions, thus generating centres of symmetry. Consequently, the overall system is non-directional (Fig. 3). This centrosymmetric packing may be due to cancellation of dipolar moments.

In conclusion, the unsymmetrical ligand **1** based on two different coordination poles was shown to form a directional 1-D coordination network in the presence of $CoCl_2$ demonstrating the viability of the approach. The network was structurally characterised by X-ray diffraction methods on single crystals.

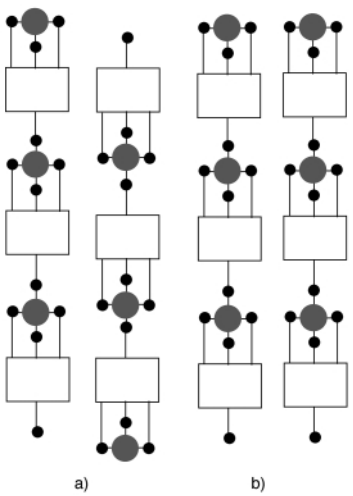


Fig. 2 Schematic representation of consecutive directional 1-D networks leading to symmetrical (a) or unsymmetrical (b) packing.

Fig. 3 A portion of the X-ray structure of the directional 1-D network showing the packing of consecutive networks in 'head to tail' fashion. H atoms and solvent molecules are not presented for clarity. For distances and angles see text.

However, the 1-D networks were packed parallel to each other with opposite orientation of linear arrays. The possibility of controlling the unsymmetrical packing of such 1-D coordination networks is currently under exploration using chiral analogues of the ligand **1**.

We thank the CNRS and the Institut Universitaire de France (IUF) for financial support.

Notes and references

† *Crystal data* for **1**: (purple, 173 K), $C_{16}H_{16}Cl_2CoN_2S_2{\cdot}2CH_3OH$, M = 494.37, orthorhombic, a = 13.3874(4), b = 13.9184(7), c = 12.0950(7) Å, U = 2253.7(3) Å^3, Z = 4, space group *Pbcn*, D_c = 1.46 g cm^{-3}, Nonius Kappa CCD, Mo-Kα, μ = 1.199 mm^{-1}, 1739 data with $I > 3\sigma(I)$, R = 0.036, Rw = 0.075. The structural determination was achieved using the Nonius OpenMolenN package.[13] CCDC 182/1762. See http://www.rsc.org/suppdata/cc/b0/b006099m/ for crystallographic files in .cif format.

1 R. Robson, in *Comprehensive Supramolecular Chemistry Vol. 6*, ed. D. D. Macnicol, F. Toda and R. Bishop, Pergamon, Oxford, 1996, p. 733; S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460.

2 M. Fujita, in *Comprehensive Supramolecular Chemistry, Vol. 9*, ed. J. P. Sauvage and M. W. Hosseini, Pergamon, Oxford, 1996, p. 253; O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; T. L. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972; J. Blake, N. R. Champness, S. S. M. Chung, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 1675; M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li and M. Schröder, *Chem. Commun.*, 1997, 2327.

3 U. Velten and M. Rehahn, *Chem. Commun.*, 1996, 2639.

4 C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton and A. White, *Angew. Chem., Int. Ed.*, 1998, **37**, 920.

5 G. Mislin, E. Graf, M. W. Hosseini, A. De Cian, N. Kyritsakas and J. Fischer, *Chem. Commun.*, 1998, 2545.

6 C. Klein, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Chem. Commun.*, 2000, 239.

7 E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1992, 3467; E. C. Constable, A. J. Edwards, D. Philips and P. R. Raithby, *Supramol. Chem.*, 1995, **5**, 93.

8 S. J. Loeb and G. K. H. Shimizu, *Chem. Commun.*, 1993, 1395; M. Ferigo, P. Bonhôte, W. Marty and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, 1994, 1549; A. Neels, B. Mathez Neels and H. Stoeckli-Evans, *Inorg. Chem.*, 1997, **36**, 3402.

9 M. Loï, E. Graf, M. W. Hosseini, A. De Cian and J. Fischer, *Chem. Commun.*, 1999, 603; M. Loï, M. W. Hosseini, A. Jouaiti, A. De Cian and J. Fischer, *Eur. J. Inorg. Chem.*, 1999, 1981.

10 H. Takalo and J. Kankare, *Acta Chem. Scand., Ser. B*, 1987, **41**, 219.

11 H. Takalo, P. Pasanen and J. Kankare, *Acta Chem. Scand. Ser. B*, 1988, **42**, 373.

12 L. della Ciana and A. Haim, *J. Heterocycl. Chem.*, 1984, **21**, 607.

13 OpenMolenN, Interactive Structure Solution, Nonius B.V., Delft, The Netherlands, 1997.