2,2′-Bi-1,6-naphthyridine metal complexes: a new ligand and a novel 2 × 2 inclined interpenetration of (4,4) nets or formation of helicoidal chains†

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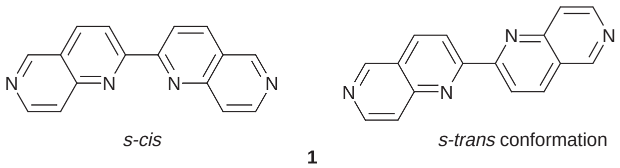
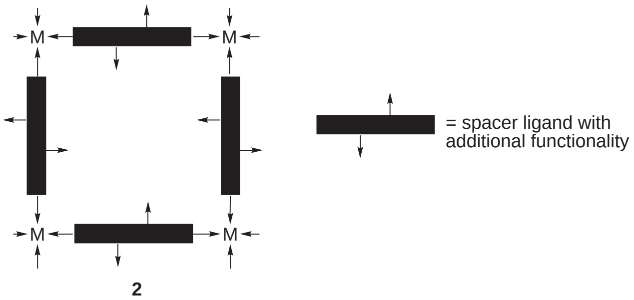
Cobalt(II), zinc(II) and cadmium(II) salts react with the new spacer ligand 2,2′-bi-1,6-naphthyridine 1 to give 2D-planar (4,4) frameworks which interpenetrate such that each grid window of each sheet has two other sheets passing through it with all sheets being equivalent whereas copper(I) tetrafluoroborate and 1 form a 2_1-helicoidal chain with neigboring chains interlocking through an aromatic π–π interaction.

The synthesis of interpenetrating nets and the elucidation of the factors leading to a periodic entanglement is an area of increasing interest.[1] Many interpenetrating structures were obtained from attempts to create porous solid bases on metal coordination polymers.[2] As nature tends to avoid vacuum, identical copies of the frameworks with large openings interpenetrate to fill this empty space rather than to create a single network.[3] In the design of metal–ligand networks rigid and multidentate ligands with pyridine groups feature prominently as building blocks.[4] In our study of functionalized 2,2′-bipyridine-type ligands[5] we look here at the self-assembly process of the new spacer 2,2′-bi-1,6-naphthyridine **1**[6] with various metal salts.



1

The choice of functionalized 2,2′-bipyridine building blocks stems from the aim to supply functional groups within the inner walls of a porous coordination polymer as is schematically depicted in **2**. Such functionalities should eventually interact with organic guest molecules, *e.g.* through hydrogen bonding, or allow for the anchoring of additional metal ions.



2

Spacer **1** reacts with cobalt chloride, zinc or cadmium perchlorate in the presence of a slight excess of KSCN in water–ethanol (1 : 1) to give well formed crystals in yields of 50% and above. The products were investigated by single crystal X-ray analysis† and correspond to the formula $^2_\infty[M(NCS)_2(\mu\text{-}\mathbf{1})_2]$ (M = Co, Zn, Cd) (matching the C,H,N analytical data‡). The three M(II) compounds are isostructural. The binaphthyridine ligand assumes the *s-trans* conformation and bridges between the metal centers. Four ligands of **1** are arranged around the metal in a square-planar fashion and two *trans* (nitrogen-bound) isothiocyanato ligands complete the octahedral metal coordination sphere. The bonded metal–**1** arrangement leads to planar (4,4) nets. Fig. 1 shows an individual metal–ligand grid. The bridged metal–metal distances along the edges of the parallelograms are around 15.76–16.05 Å and the distances along the shorter and longer diagonals are 21.44–21.95 and 23.10–23.43 Å, respectively, depending on the metal. The 2D framework from Fig. 1 is interpenetrated in an inclined mode[1] by symmetry related, identical sheets to give an interlocked 3D structure. The manner of interpenetration is such that each window of each grid has parts of two other sheets passing through it, which we would like to call a 2 × 2 interpenetration (Figs. 2 and 3). It was surprising at first that the rings were large enough and the binaphthyridine rods slim enough to allow the passage of two sheets, when considering the van der Waals surfaces of the aromatic system and the NCS group. A space-

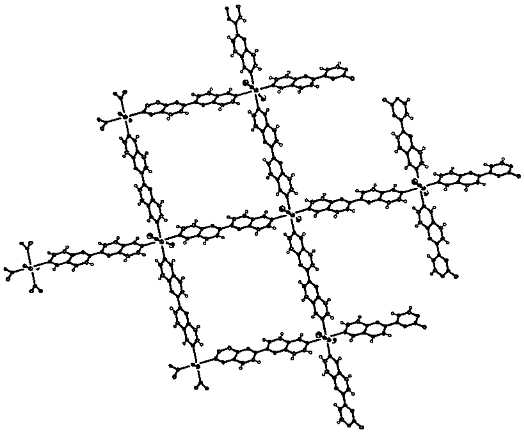


Fig. 1 View of a section of the planar individual metal–ligand network in $^2_\infty[M(NCS)_2(\mu\text{-}\mathbf{1})_2]$ (M = Co, Zn, Cd).

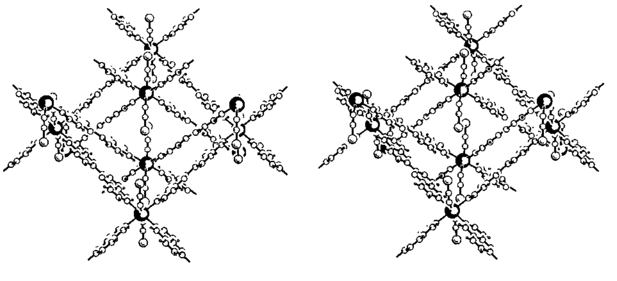


Fig. 2 Stereoview along *b* of the interpenetration of parts of two sheets through a grid window in $^2_\infty[M(NCS)_2(\mu\text{-}\mathbf{1})_2]$ (M = Co, Zn, Cd).

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† Dedicated to Professor Dr Bernt Krebs on the occasion of his 60th birthday.

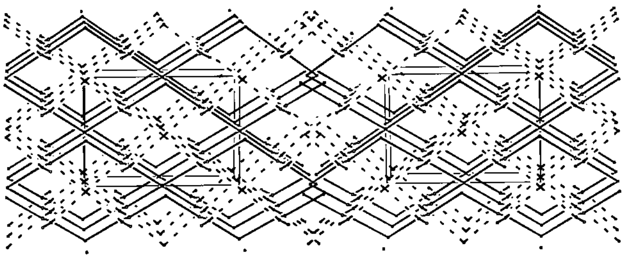

Fig. 3 Stereoview along *c* of the schematic framework of $^{2}_{\infty}$[M(NCS)$_2$(μ-**1**)$_2$] (M = Co, Zn, Cd), with only the metal center and the central C–C unit of the binaphthyridine moiety shown. Sheets of different inclination are drawn with solid or dashed lines, respectively.

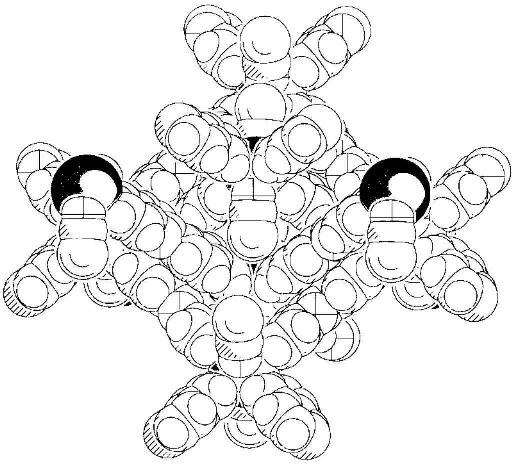

Fig. 4 Space-filling drawing of the interpenetration of parts of two sheets through a grid window in $^{2}_{\infty}$[M(NCS)$_2$(μ-**1**)$_2$] (M = Co, Zn, Cd).

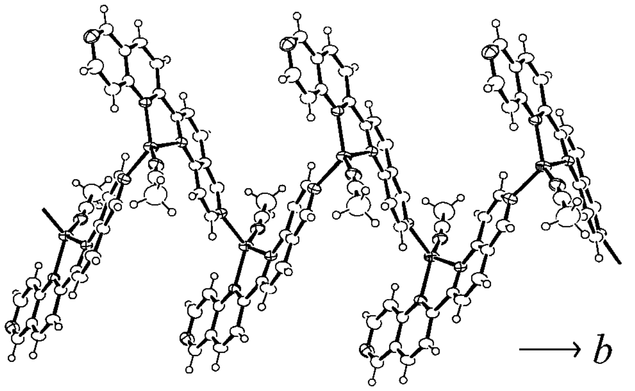

Fig. 5 Section of the 2$_1$-helical coordination polymer of $^{1}_{\infty}$[Cu(MeCN)(μ-**1**)]BF$_4$·0.5CH$_2$Cl$_2$. Anion and solvent molecule have been omitted for clarity.

filling model then illustrated the close π–π contact of the naphthyridine moieties (Fig. 4). The knots or metal centers of the intersecting networks do not lie within the plane of the pierced ring but above and below. The nets run either parallel to the (021) or to the (02 − 1) plane. The inclination of the sheets is almost perpendicular, the angle ranges from 92.9° for the cobalt to 93.7° for the cadmium grids. A similar mode of interpenetration was so far only reported in the structure of [Cd(py)$_2${Ag(CN)$_2$}$_2$],[7] for the more common type of a 1 × 1 interpenetration in (4,4) square grid sheets, the structure of $^{2}_{\infty}$[M(4,4′-bipy)$_2$]SiF$_6$ (M = Zn, Cd) is a typical example.[8]

The anellated arene substituents in the α position to the bipyridine nitrogen donor atoms prevent the chelating coordination of two or three ligands of **1** with its bipyridine unit in an octahedral complex. A bipyridine selectivity in **1** (cuproin group) can, however, be expected towards copper(I). An X-ray study† revealed that the reaction of **1** with [Cu(MeCN)$_4$]BF$_4$ in MeCN–CH$_2$Cl$_2$ led to a compound of formula $^{1}_{\infty}$[Cu(MeCN)(μ-**1**)]BF$_4$·0.5CH$_2$Cl$_2$. A 1D-coordination polymer (Fig. 5) originates from the chelation of the copper center by **1** in its *s-cis* conformation together with the bridging action of the ligand to the next metal through one of its exodentate nitrogen donors. The distorted tetrahedral coordination sphere at copper is completed by an acetonitrile ligand. The copper–ligand strand assumes a helicoidal conformation following a 2$_1$ screw axis. The neighboring parallel strands are of opposite helicity and interlock (interdigitate) through π–π interactions of the extended aromatic binaphthyridine system.

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Notes and references

† *Crystal data*: $^{2}_{\infty}$[Co(NCS)$_2$(μ-**1**)$_2$], orthorhombic, space group *Cmca*, a = 21.4385(17), b = 15.918(1), c = 8.3683(5) Å, V = 2855.8(3) Å^3, Z = 4, D_c = 1.6087, final R, wR values 0.0321, 0.0744 for 1334 independent reflections with $I > 2\sigma(I)$.

$^{2}_{\infty}$[Zn(NCS)$_2$(μ-**1**)$_2$], orthorhombic, space group *Cmca*, a = 21.5003(19), b = 15.925(1), c = 8.3967(5) Å, V = 2875.0(4) Å^3, Z = 4, D_c = 1.6129, final R, wR values 0.0269, 0.0744 for 1555 independent reflections with $I > 2\sigma(I)$.

$^{2}_{\infty}$[Cd(NCS)$_2$(μ-**1**)$_2$], orthorhombic, space group *Cmca*, a = 21.9537(13), b = 16.027(1), c = 8.5477(5) Å, V = 3007.5(3) Å^3, Z = 4, D_c = 1.6457, final R, wR values 0.0235, 0.0606 for 1679 independent reflections with $I > 2\sigma(I)$.

$^{1}_{\infty}$[Cu(MeCN)(μ-**1**)]BF$_4$·0.5CH$_2$Cl$_2$, monoclinic, space group *C*2/*c*, a = 22.4063(16), b = 8.1045(4), c = 22.5896(18) Å, V = 4029.8(5) Å^3, Z = 8, D_c = 1.624(2), final R, wR values 0.0358, 0.0797 for 2754 independent reflections with $I > 2\sigma(I)$.

Data collection by the ω-scan method, Mo-Kα radiation (λ = 0.71073), graphite monochromator, at 200 K on a STOE IPDS diffractometer. Structure solution by direct methods (SHELXS-97)[9] and refined by full-matrix least-squares on F^2 (SHELXL-97);[9] all non-hydrogen positions found and refined with anisotropic temperature factors. Graphics were obtained with ORTEP3 and PLUTON for Windows.[10] CCDC 182/1024. See http://www.rsc.org/suppdata/cc/1998/2637/ for crystallographic files in .cif format.

‡ *Elemental analyses*: $^{2}_{\infty}$[Co(NCS)$_2$(μ-**1**)$_2$] calc. C 59.04, H 2.89, N 20.26; found C 58.68, H 2.92, N 20.22%. $^{2}_{\infty}$[Zn(NCS)$_2$(μ-**1**)$_2$] calc. C 58.49, H 2.89, N 20.06; found C 58.16, H 2.81, N 20.00%. $^{2}_{\infty}$[Cd(NCS)$_2$(μ-**1**)$_2$] calc. C 54.81, H 2.68, N 18.81; found C 54.95, H 2.74, N 19.10%. $^{1}_{\infty}$[Cu(MeCN)(μ-**1**)]BF$_4$·0.5CH$_2$Cl$_2$ calc. C 35.96, H 2.03, N 11.10; found C 35.77, H 2.18, N 11.08%.

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