

Co-ordination engineering: when can one speak of an “understanding”? Case study of the multidentate ligand 2,2'-dimethyl-4,4'-bipyrimidine †

Christoph Janiak,^{*a} Lars Uehlin,^a He-Ping Wu,^a Peter Klüfers,^{*b} Holger Piotrowski^b and Tobias G. Scharmann^c

^a Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany. E-mail: janiak@uni-freiburg.de

^b Institut für Anorganische Chemie, Universität Karlsruhe, Kaiserstr. 12, D-76131 Karlsruhe, Germany

^c Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

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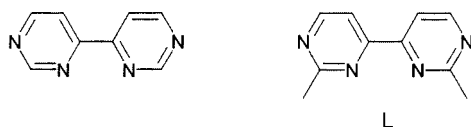
The mode of co-ordination of the multidentate ligand 2,2'-dimethyl-4,4'-bipyrimidine (L) was found to depend on the metal ion, the crystallization conditions, the metal-to-ligand ratio, and the anion. With nickel a chelating co-ordination through the *endo*-dentate nitrogen donor set is observed in the molecular complex [NiCl₂(L)(H₂O)]·CH₃NO₂, derived from hot CH₃NO₂. With Cu(NO₃)₂ and CuI–CH₃CN one- and two-dimensional (1-D and 2-D) co-ordination polymers of formula $\frac{1}{2}$ [Cu(NO₃)₂(μ-L)] and $\frac{2}{3}$ [Cu₂(μ₃-I)₂(μ-L)] are obtained, where the bipyrimidine ligand is solely bridging through the two *exo*-dentate nitrogen atoms. On the other hand, a synthesis from CuI and crystallization from hot dimethyl sulfoxide leads to a 1-D iodide-bridged co-ordination polymer $\frac{1}{2}$ [Cu(μ-I)(L)] with a chelating ligand. With AgNO₃ two different types of co-ordination polymers were found, depending on the silver-to-ligand ratio. At a 1 : 1 ratio in the presence of a co-ordinating anion a 2-D network, $\frac{2}{3}$ [Ag(μ-NO₃)₂(μ-L)], with only bridging bipyrimidine ligands is observed. At a metal excess, a 3-D framework, $\frac{3}{2}$ [Ag₃(μ₃-NO₃)₃(μ₃-L)₂], forms where L functions both as a chelating and as bridging ligand. A tetradentate co-ordination mode of L towards silver is also found with non-co-ordinating anions, such as BF₄⁻ and PF₆⁻, and gives rise to the isostructural 2-D co-ordination polymers of formula $\frac{2}{3}$ [Ag₃(CH₃CN)₃(μ₃-L)₂]X₃ (X = BF₄ or PF₆).

Introduction

Metal complexes of chelating 2,2'-bipyridine or bridging 4,4'-bipyridine or hydrogen-substituted derivatives thereof are of constant and general interest in metal co-ordination chemistry.¹ The latter has recently gained considerable interest in the synthesis of (rectangular) two-dimensional network structures.² The generation of such frameworks is a promising path in the search for stable microporous metal–organic networks that exhibit reversible guest exchange and possibly selective catalytic activity.³



In view of the large use of heterocyclic bipyridine ligands, it is remarkable that the related 2,2'-bipyrimidine ligand or its derivatives, such as 2,2'-dimethyl-4,4'-bipyrimidine (L), have so far rarely been employed in metal co-ordination chemistry.^{4–6}



These ambi- or multi-dentate bipyrimidine ligands can be thought of combining the ligating properties of the chelating and bridging bipyridine ligands. The idea behind the use of such ambidentate ligands is to have tetrahedral building blocks for co-ordination polymers⁷ based on the *endo*-chelation of two ligands with an appropriate metal center (1) or to supply functional donor atoms within the walls of the co-ordination polymer when the ligands are solely *exo*-bridging (2). Such functionalities should eventually interact with organic guest molecules, *e.g.* through hydrogen bonding, or allow for the anchoring of additional metal ions.

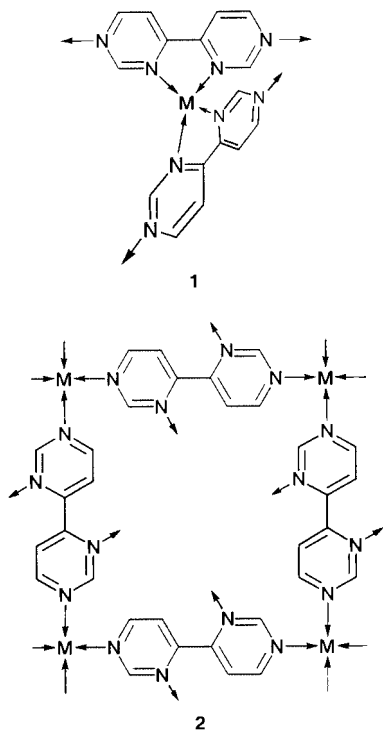
Our research has been concerned with the utilization of multidentate *endo*-chelating/*exo*-bridging modified 2,2'-bipyridine ligands such as 2,2'-bi-1,6-naphthyridine⁸ or 5,5'-dicyano-2,2'-bipyridine⁹ and ligands of the tris(pyrazolyl)borate type for the assembly of metal co-ordination polymers.¹⁰

In this paper the ligand 2,2'-dimethyl-4,4'-bipyrimidine (L) serves as an example to derive a more profound understanding in the co-ordination engineering with multidentate ligands, as a part of crystal engineering. We describe the results of synthetic and structural studies of metal salts with L and try to elucidate the factors which lead to bridging or chelating or simultaneous bridging/chelating co-ordination. Through the use of a variety of metal centers and crystallization conditions we want to explore a large section of the energy hypersurface of ligands in co-ordination chemistry.

An understanding of the self-assembly process between metal ions and flexible, multidentate ligands is a contemporary goal in supramolecular co-ordination chemistry.¹¹ While rigid bidentate ligands, for example, allow only for one result in the metal co-ordination process, flexible and multidentate ligands

Dedicated to Professor Dr Heinrich Vahrenkamp on the occasion of his 60th birthday.

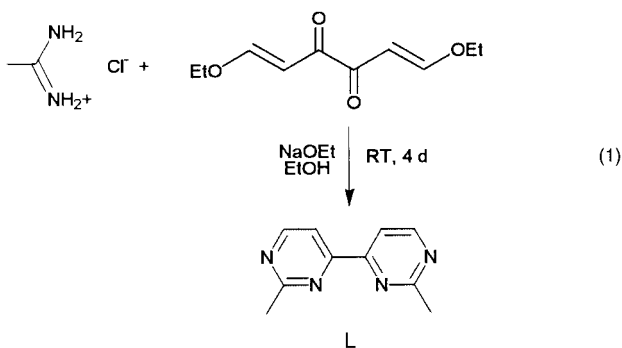
† Supplementary data available: X-ray powder diffractograms. Available from BLDSC (No. SUP 57608, 4 pp.). See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).



can give two or more metal structures with the same stoichiometry. This has been termed an “inorganic supramolecular library” or “virtual combinatoric library” by Lehn and co-workers.¹² It is not yet possible to predict the product in these cases. The structure can be determined by subtle factors such as π - π stable interactions between the ligands or by the anions.

Results and discussion

The ligand 2,2'-dimethyl-4,4'-bipyrimidine (L) was prepared following a slightly modified literature procedure by Effenberger.^{13,14} The reaction of acetamidinium hydrochloride with 1,6-bis(ethoxy)hexa-1,5-diene-3,4-dione gave L in 42% yield, eqn. (1). The structure of L is shown in the *s-cis* conformation



which is the appropriate conformer for chelate formation. A structure determination in the solid state revealed the *s-trans* conformation of the pyrimidine rings. A semiempirical PM3 calculation in vacuum and in chloroform supported the assignment of the *s-trans* form as the preferred conformation.¹⁴

The aim in the syntheses of the transition metal complexes of L was to obtain single crystals suitable for X-ray diffraction. The diffusion technique was generally used: a solution of the ligand was overlaid with a solution of the metal salt. Scheme 1 summarizes the reactions and products which are described in more detail below.

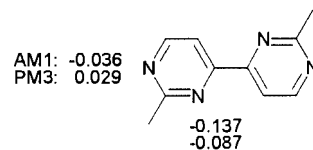
Fig. 1 gives a schematic overview on the structural results which are systematically arranged according to the following interpretation which we propose. There are four principal co-

ordination modes of the ambidentate bipyrimidine ligand: bidentate chelating, bidentate bridging, tridentate, and tetradentate. The tridentate mode has been observed before,⁶ the other three are presented here. Generally, a bridging coordination mode gives rise to a one-dimensional metal–ligand substructure. Bridge formation together with metal chelation results in a two-dimensional metal–ligand substructure. Depending on the anion, both types of substructures can then be connected further to a two- or three-dimensional framework, respectively.

The major determinant for the co-ordination mode of L appears to be the type of metal ion. With nickel(II) only the bidentate chelating mode was elucidated (complex 4, $[\text{NiCl}_2(\text{L})(\text{H}_2\text{O})]\cdot\text{CH}_3\text{NO}_2$). Copper(II) was only found in the bidentate bridging mode (5, $[\text{Cu}(\text{NO}_3)_2(\mu\text{-L})]$). Towards copper(I) and silver(I) more than one co-ordination mode was observed here, so that there was an opportunity to check for additional variables.

Bidentate chelating versus bidentate bridging in the case of copper(I): influence of crystallization conditions (cf. Fig. 1)

For copper(I) the co-ordination mode can be controlled through the thermodynamic crystallization conditions. Crystallization from a hot solution or after thermal treatment leads to a chelate complex 8, $[\text{Cu}(\mu\text{-I})(\text{L})]$. When the whole synthesis and crystallization procedure is carried out at room temperature a ligand-bridged co-ordination polymer is obtained in complex 7, $[\text{Cu}_2(\mu_3\text{-I})_2(\mu\text{-L})]$. These conclusions for the case of copper(I) are supported through the crystallization conditions of the other examples. The nickel chelate structure 4 was crystallized from hot CH_3NO_2 . The copper(II) and silver(I) co-ordination polymers 5 and 9, respectively, were crystallized at room temperature. The origin of these differences may lie in the conformational *s-trans* preference of L together with a charge difference of the nitrogen donors. An AM1 or PM3 theoretical calculation¹⁵ assigns a higher negative charge to the *endo*-dentate nucleophiles. Other orbital interactions of the nitrogen donors being equal, a higher negative charge leads to a thermodynamically more stable electrostatic interaction with the metal.^{10,16} At the same time, the resulting chelate co-ordination requires the ligand to assume the less preferred *s-cis* conformation. A competitive thermodynamic versus kinetic control may also be invoked in the assembly process.¹⁷



A tridentate co-ordination mode of copper(I) with L was described earlier in the compound $[\text{Cu}_2(\text{CH}_3\text{CN})_2(\mu\text{-L})][\text{PF}_6]_2$.⁶ There, the participation of one *exo*- and both *endo*-nitrogen donors yields an infinite helicoidal polymeric chain around a 2_1 axis. This difference to the copper(I)–bipyrimidine–iodine structures 7 and 8 can be traced to the change in the anion: co-ordinating iodine versus “non”-co-ordinating hexafluorophosphate (see below).

Bidentate bridging versus tetradentate in the case of silver(I): influence of the metal-to-ligand ratio and of the anion (cf. Fig. 1)

Among the metals examined, only silver(I) was found capable of occupying all four donor atoms of L in metal co-ordination, as shown by the structures of 10 through 12. At the same time this appears to be the favored co-ordination mode for silver. In order to have only the *exo*-dentate nitrogen donor set of L co-ordinating to silver(I) a 1 : 1 metal-to-ligand ratio has to be employed in the presence of a co-ordinating (nitrate) anion.

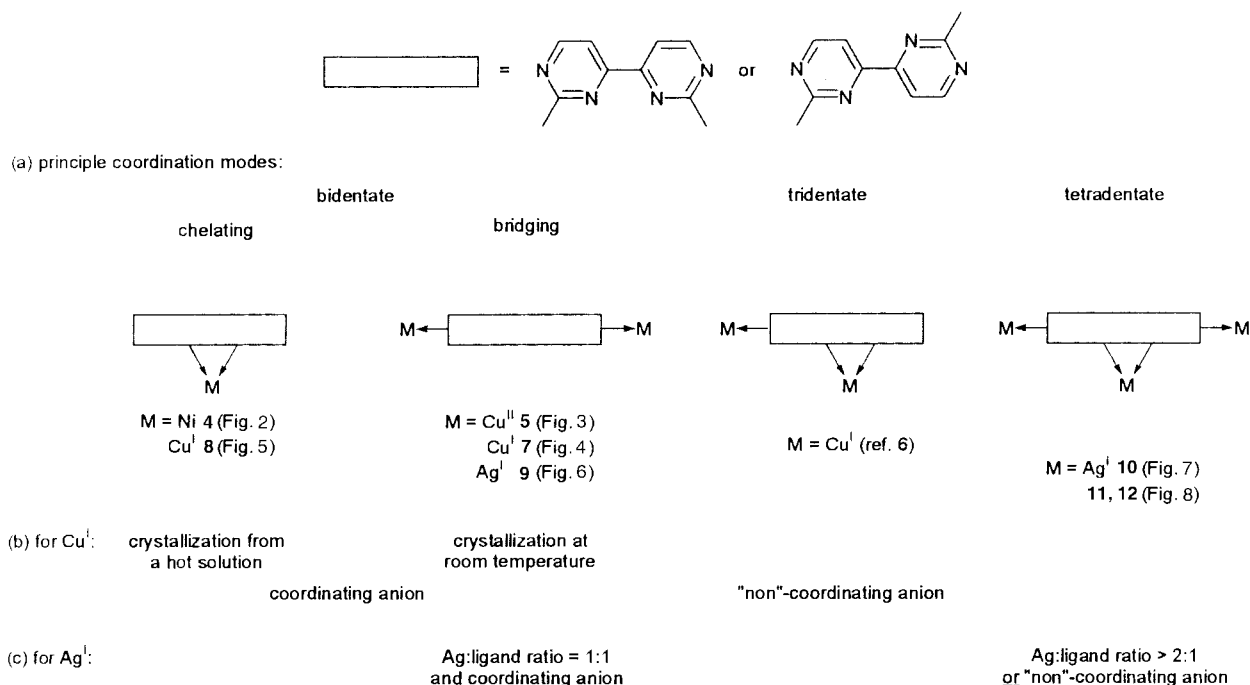
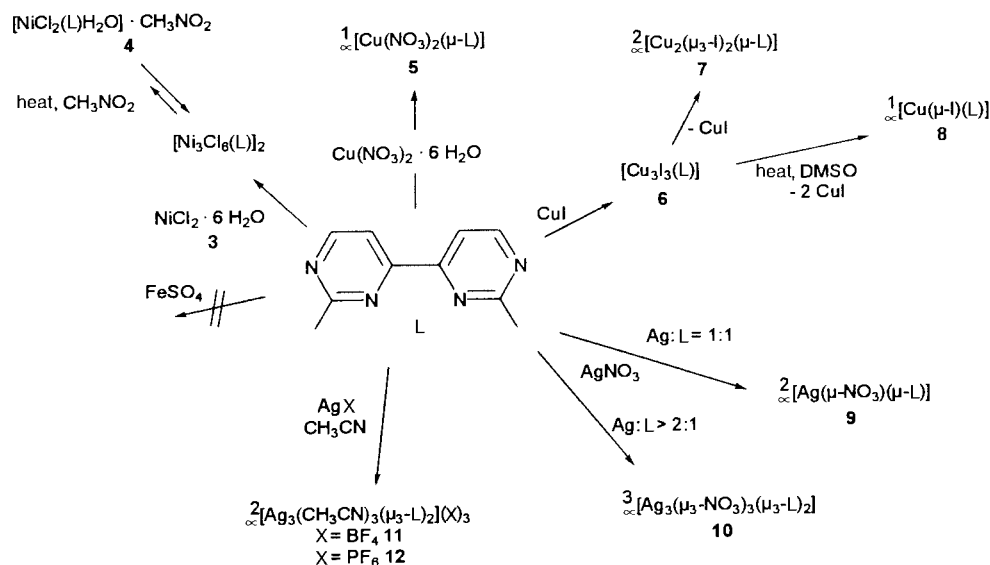


Fig. 1 Schematic presentation of the co-ordination modes of 2,2'-dimethyl-4,4'-bipyrimidine (L) towards different metal centers (a) together with a brief indication on the proposed underlying determining variables for copper(I) (b) and silver(I) (c).



Scheme 1 Overview of the metal complex formation reactions of L with nickel, copper, and silver salts.

Then one derives the structure of **9**, ${}_{\infty}^2[\text{Ag}(\mu\text{-NO}_3)(\mu\text{-L})]$, with solely bridging co-ordination. Otherwise, if an excess of silver was used in the case of the NO_3^- anion, tetradentate co-ordination was achieved. The structure of **10**, ${}_{\infty}^3[\text{Ag}_3(\mu_3\text{-NO}_3)_3(\mu_3\text{-L})_2]$, is the example. An obvious variable in the silver structures is the anion.^{18,19} In the networks of **9** and **10** the co-ordinating nitrate anion plays a dominant role in the connectivity of the framework.

To check for the influence of the anion, the "non"-co-ordinating counter ions BF_4^- and PF_6^- were employed as their silver salts as starting materials. The crystalline products **11** and **12**, ${}_{\infty}^2[\text{Ag}_3(\text{CH}_3\text{CN})_3(\mu_3\text{-L})_2]\text{X}_3$, from AgBF_4 and AgPF_6 , respectively, were found to be isostructural.^{9,18b,20} The structures exhibit the tetradentate co-ordination mode. The result did not depend on the metal-to-ligand ratio here, which was 1:1 in the case of $\text{X} = \text{BF}_4^-$ (**11**) and 2:1 for $\text{X} = \text{PF}_6^-$ (**12**). Thus, for a 1:1 metal-to-ligand ratio the co-ordination of L to silver can be controlled by the counter ion.

The above relations are not meant to imply that we have

reached a full understanding. Matters may still be more complicated in view of the large number of parameters in a crystallization experiment. However, we feel that we can provide some guidelines and rationalizations which should be applicable at least for similar tetradentate chelating/bridging ligands. The individual structures are briefly described in more detail in the following.

[NiCl₂(L)(H₂O)]·CH₃NO₂ **4.** Fig. 2 illustrates the molecular structure of aquadichloro(2,2'-dimethyl-4,4'-bipyrimidine)-nickel(II): a chelate complex with *s-cis* conformation of the pyrimidine rings. A somewhat unusual trigonal-bipyrimidal geometry around nickel(II) is found,²¹ with the stronger nitrogen and oxygen donor atoms in the equatorial plane. The weaker chloride ions occupy the axial sites. Apparently, the methyl groups prevent the formation of an octahedral co-ordination polyhedron. A nitromethane molecule is incorporated in the lattice but with distances larger than 3 Å from the metal atom.

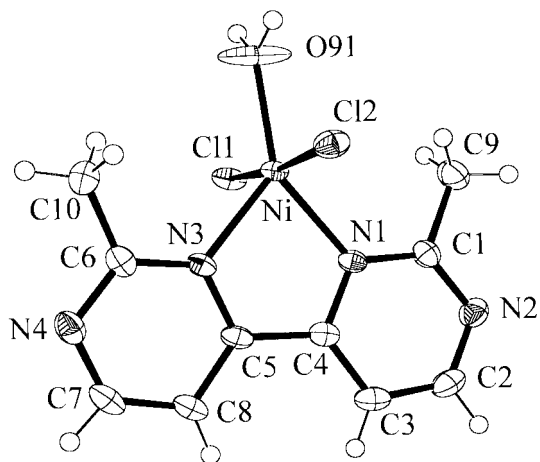


Fig. 2 Molecular structure of $[\text{NiCl}_2(\text{L})(\text{H}_2\text{O})]$ **4**. Selected distances [Å] and angles [°]: Ni–N(1) 2.010(2), Ni–N(3) 2.010(2), Ni–O(91) 1.957(3), Ni–Cl(1) 2.3441(7) and Ni–Cl(2) 2.3234(8); O(91)–Ni–N(1) 146.00(14), O(91)–Ni–N(3) 133.45(14), O(91)–Ni–Cl(1) 85.86(7), O(91)–Ni–Cl(2) 87.59(7), N(1)–Ni–N(3) 80.40(9), N(1)–Ni–Cl(1) 90.36(6), N(1)–Ni–Cl(2) 93.16(6) and Cl(1)–Ni–Cl(2) 172.60(3).

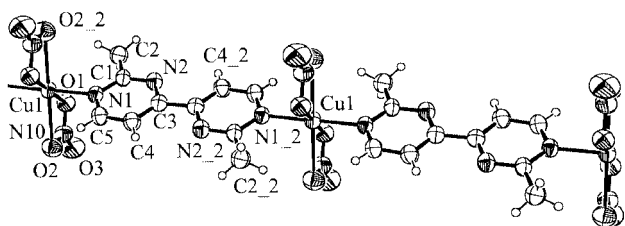


Fig. 3 Section of the linear chain structure of $[\text{Cu}(\text{NO}_3)_2(\mu\text{-L})]$ **5**. Selected distances [Å] and angles [°]: Cu–N(1), N(1)₂ 2.051(4), Cu–O(1), O(1)₂ 2.032(4) and Cu–O(2), O(2)₂ 2.531(6); O(1)–Cu–O(1)₂ 180, N(1)–Cu–N(1)₂ 180, O(1)–Cu–N(1) 91.0(2), O(1)₂–Cu–N(1) 89.0(2), O(1)–Cu–N(1)₂ 89.0(2), O(1)₂–Cu–N(1)₂ 91.0(2), O(1)–Cu–O(2)₂ 123.3(2), O(1)–Cu–O(2) 56.7(2), N(1)–Cu–O(2)₂ 90.9(2), N(1)₂–Cu–O(2)₂ 89.1(2), O(1)₂–Cu–O(2)₂ 56.7, O(1)₂–Cu–O(2) 123.3(2), N(1)–Cu–O(2) 89.1(2), N(1)₂–Cu–O(2) 90.9(2), O(2)₂–Cu–O(2) 180, O(2)–N(10)–O(1) 117.5(4), O(3)–N(10)–O(1) 118.4(5) and O(3)–N(10)–O(2) 124.2(5) (symmetry equivalent position ₂ $-x + 1, -y + 1, -z + 1$).

$[\text{Cu}(\text{NO}_3)_2(\mu\text{-L})]$ **5**. A crystal structure determination showed that the bipyrimidine ligand bridges between two copper centers with its *exo*-dentate nitrogen atoms to give a linear –Cu–L–Cu–L– chain, which is indicated in Fig. 3. The *endo*-dentate donor atoms of L are not involved in metal co-ordination and the ligand assumes the *s-trans* conformation. Two chelating nitrate ions complete the Jahn–Teller-distorted pseudo-octahedral co-ordination sphere of the copper centers. The Jahn–Teller distortion is along two *trans* Cu–O contacts, one to each of the nitrate ligands. The small bite angle of the nitrate anions leads to a considerable distortion of the octahedral co-ordination polyhedron.

$[\text{Cu}_2(\mu_3\text{-I})_2(\mu\text{-L})]$ **7**. Fig. 4 illustrates the two-dimensional co-ordination polymer of this compound.²² The ligand assumes the *s-trans* conformation and bridges with its *exo*-dentate nitrogen atoms between two kinked copper iodide double strands. The CuI substructure is an infinite stair polymer in which each iodide is surrounded by three metal atoms and each copper in turn by three iodide ions. Analogous structures can be found in CuI compounds with pyridine, 2-methylpyridine and 2,4-dimethylpyridine.^{23,24} The stairs run parallel to the crystallographic *c* axis. The double strands can be thought of being built from planar parallelograms which are formed from two copper and two iodine atoms. The co-ordination polyhedron at copper is a distorted tetrahedron. The bipyrimidine ligands have a role

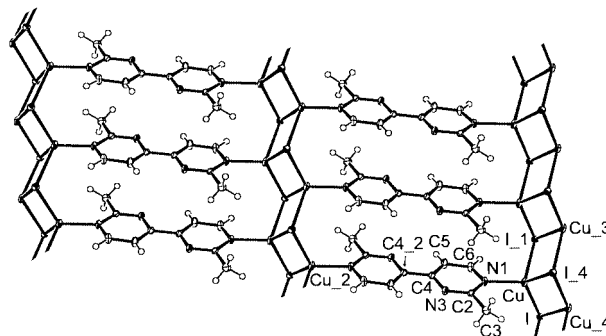


Fig. 4 Layer structure of the two-dimensional co-ordination polymer $[\text{Cu}_2(\mu_3\text{-I})_2(\mu\text{-L})]$ **7** with an infinite one-dimensional CuI stair substructure bridged by bipyrimidine ligands, viewed perpendicular to the *ab* plane. Selected distances [Å] and angles [°]: Cu–I 2.6014(7), Cu–I₄ 2.6532(7), Cu–I₁ 2.7347(8), Cu–N(1) 2.030(3), Cu⋯Cu₄ 2.649(1), Cu–I–Cu₄ 60.53(2), Cu₃–I₄–Cu₄ 103.80(2), Cu–I₄–Cu₃ 82.61(2), N(1)–Cu–I 113.3(1), N(1)–Cu–I₄ 114.5(1), N(1)–Cu–I₁ 105.03(9), I–Cu–I₄ 119.47(2), I–Cu–I₁ 103.80(2) and I₁–Cu–I₄ 97.39(2) (symmetry equivalent positions ₁ $x, y, z - 1$; ₂ $-x + 1, -y + 1, -z$; ₃ $-x + 2, -y, -z$; ₄ $-x + 2, -y, -z + 1$).

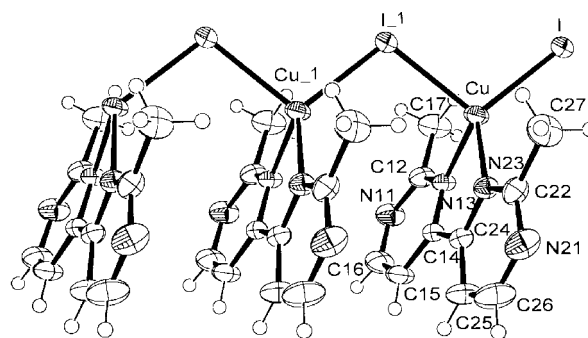


Fig. 5 Chain structure along *c* of the one-dimensional co-ordination polymer $[\text{Cu}(\mu\text{-I})(\text{L})]$ **8** with a CuI zig zag chain substructure. Selected distances [Å] and angles [°]: Cu–I 2.5374(5), Cu–I₁ 2.5937(5), Cu–N(13) 2.091(2) and Cu–N(23) 2.079(2); Cu–I₁–Cu₁–I₁ 104.049(14), N(13)–Cu–N(23) 79.45(10), N(13)–Cu–I 127.00(8), N(13)–Cu–I₁ 104.84(8), N(23)–Cu–I 122.05(10) and N(23)–Cu–I₁ 118.27(10) (symmetry equivalent position: ₁ $x, y, z + 1$).

of a spacer between the stairs and bridge the strands to a layer structure.

$[\text{Cu}(\mu\text{-I})(\text{L})]$ **8**. Fig. 5 shows the structure of this one-dimensional co-ordination polymer²² which was obtained from hot DMSO solution. The bipyrimidine ligand is in its *s-cis* conformation and chelates the copper center, as is usually found for bipyridine copper complexes.²⁵ The *exo*-dentate nitrogen atoms are not involved in metal co-ordination. The pseudo-tetrahedral co-ordination sphere of the copper ions is completed by two iodide ions so that a Cu–I zig zag chain is formed. The chain runs parallel to the crystallographic *c* axis which is also the needle axis. Similar Cu–I chains are observed with the pyridine derivatives acridine²⁶ and collidine (2,4,6-trimethylpyridine).²⁷ We note that dimeric (Cu₂I₂) or tetrameric cubane or chair/stepped cubane (Cu₄I₄) structures might have been another possibility for the arrangement of the CuI substructure.^{26,28–31}

$[\text{Ag}(\mu\text{-NO}_3)(\mu\text{-L})]$ **9**. Fig. 6 depicts the structure of the two-dimensional network of complex **9**.³² The framework can be thought of being built up from zig zag Ag–NO₃–Ag–NO₃ chains which are bridged by the bipyrimidine ligands in their *s-trans* form through the *exo*-dentate donor atoms. This bridging action of a metal–anion strand is akin to the structural motif found above in **7**.

$[\text{Ag}_3(\mu_3\text{-NO}_3)_3(\mu_3\text{-L})_2]$ **10**. The structure of the three-dimensional framework of complex **10** is shown in Fig. 7.

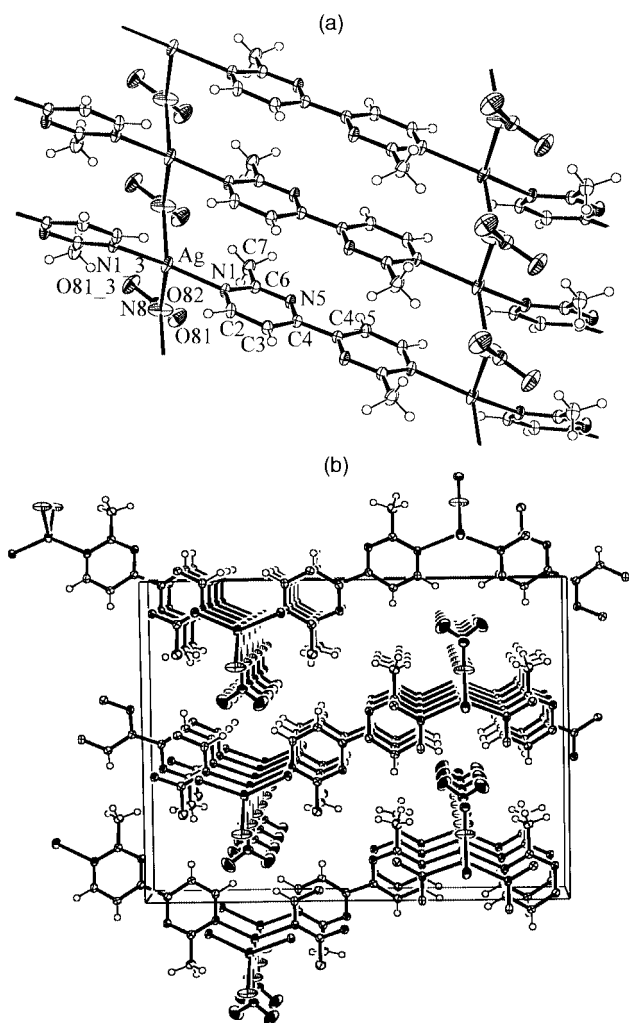


Fig. 6 Two-dimensional network of $2[\text{Ag}(\mu\text{-NO}_3)(\mu\text{-L})]_2$ **9** built from the bridging of infinite $\text{Ag-NO}_3\text{-Ag-NO}_3$ strands by the bipyrimidine ligands. (a) View perpendicular to a layer section (along b), (b) view along the layers (along a). Selected distances [Å] and angles [°]: $\text{Ag-N}(1), \text{N}(1)\text{-}_3$ 2.246(2) and $\text{Ag-O}(82)$ 2.449(3); $\text{N}(1)\text{-Ag-N}(1)\text{-}_3$ 137.0(1), $\text{N}(1)\text{-Ag-O}(82)$ 120.03(5) and $\text{N}(1)\text{-}_3\text{-Ag-O}(82)$ 87.59(7) (symmetry equivalent positions $\text{-}_3 -x, y, -z + 1/2$; $\text{-}_5 -x + 1, -y + 1, -z + 1$).

The structure is an example where L serves both as a chelating and as a bridging ligand at the same time, thereby utilizing all four donor atoms in metal co-ordination (*cf.* **1**). The structure contains three crystallographically different types of silver centers. Two metal atoms, Ag1 and Ag2, are similarly chelated by two bipyrimidine ligands, each, in a four-co-ordinate strongly distorted environment in between a tetrahedral and a square-planar co-ordination sphere (*cf.* Fig. 7a). The dihedral angles between the two five-membered chelate rings are 48.7(4)° for Ag1 and 51.7(5)° for Ag2. The remaining type of silver atom, Ag3, is five-co-ordinate (*cf.* Fig. 7b). The axial positions of the trigonal-bipyramidal co-ordination polyhedron are occupied by two *exo*-dentate nitrogen atoms of two bridging bipyrimidine ligands. The equatorial positions are filled by oxygen atoms of three nitrate groups which bridge between three such silver centers of the same type. The structure of **10** can be viewed as being built by the distorted tectons **1** which are bridged again by metal centers. The ligating action of L towards Ag1 and Ag2 together with the *exo* co-ordination towards Ag3 yields bipyrimidine–silver–bipyrimidine sandwich layers which are connected to a three-dimensional network through the nitrate bridges between the Ag3 centers. In an alternative view, the structure can be thought of being built from linear Ag3–bipyrimidine chains. These chains run criss-cross parallel to the ab plane and are connected by the Ag1 and

Ag2 centers as well as by the nitrate bridges (*cf.* Fig. 7c). Two additional nitrate positions complete the structure; they have only long-distance contacts to the co-ordination-polymeric part of the structure, though, and, therefore, are strongly disordered.

$2[\text{Ag}_3(\text{CH}_3\text{CN})_3(\mu_3\text{-L})_2]\text{X}_3$ with $\text{X} = \text{BF}_4$ (**11**) or PF_6 (**12**). The two-dimensional grid structures are illustrated in Figs. 8 and 9. The counter ions are in part disordered in both cases. As in the structure of **10**, also in **11** and **12** each bipyrimidine ligand is again serving as a chelating and as a bridging group using all four of its nitrogen donors. The complexes contain two different sets of silver centers. The co-ordination sphere of the four-co-ordinated Ag1 atoms is constructed from two *endo*-dentate nitrogen donors of a chelating bipyrimidine ligand, an *exo*-nitrogen donor of a bridging group and an acetonitrile molecule. The environment of Ag2 is three-co-ordinate and made up of two *exo*-dentate nitrogen donor atoms from bridging bipyrimidine ligands and a CH_3CN molecule. In a different perspective, the structures can also be thought of as being built up from a helicoidal one-dimensional co-ordination polymer based on the Ag1–ligand units (see shaded ligands in Fig. 8). This helix follows the 2_1 screw axis parallel to b (running vertical in Fig. 8). At the rims of these ribbons there are Ag2 centers, which link the adjacent helical strands.

NMR spectroscopy

The nickel and copper(II) compounds **3**, **4** and **5** as well as the silver compounds **9** and **10** were soluble in dimethyl sulfoxide and the solutions investigated by proton and carbon-13 NMR. The NMR data are included in Table 1. The spectra are similar in their chemical shifts and resemble the spectra of the “free” ligand. This is evidence that the co-ordination polymeric framework degrades. Especially, since the spectra with the paramagnetic metal centers Ni^{II} and Cu^{II} neither show a pronounced broadening nor a considerable chemical shift difference, as would be expected if the ligand remained bound to the metal ions. The slight broadening of the signal of H6 and the disappearance of the coupling to H5 and H6 is probably due to the presence of the paramagnetic ions in solution. In the spectra of the diamagnetic silver salts the coupling is retained. The peak assignment is as given for the free 2,2'-dimethyl-4,4'-bipyrimidine ligand L (*cf.* footnote to Table 1).

Infrared spectroscopy

The vibrational spectroscopy data was interpreted with the help of results from pyrimidine,³³ 2-methylpyrimidine,³⁴ and bipyridine³⁵ ligands and complexes. Most bands of 2,2'-dimethyl-4,4'-bipyrimidine L show a small shift upon complexation. The ring vibrations at 1575 and 1445 cm^{-1} show a bathochromic shift (to smaller wavenumbers) of up to 40 cm^{-1} , in part together with band splitting. The out-of-plane deformation at 770 cm^{-1} experiences a bathochromic shift between 8 and 20 wavenumbers. The in-plane vibrations at 840, 655 and 588 cm^{-1} are shifted from 5 to 15 cm^{-1} to higher wavenumbers. Similar shifts of these aforementioned so-called metal-sensitive vibrations were observed for pyrimidine and bipyridine metal complexes.^{33,35}

Conclusions

In the multidentate ligand 2,2'-dimethyl-4,4'-bipyrimidine (L) both the *endo*- and *exo*-dentate nitrogen atoms can function as donors towards metal centers. The choice of co-ordination was found to depend first on the type of metal. For a given metal center the mode of co-ordination can further be influenced through the thermal crystallization conditions, the anion and the metal-to-ligand ratio as was exemplified for copper(I) and silver(I). Solvent control might be another unexplored variable.³⁶ For copper(I) it is shown how the thermal crystallization

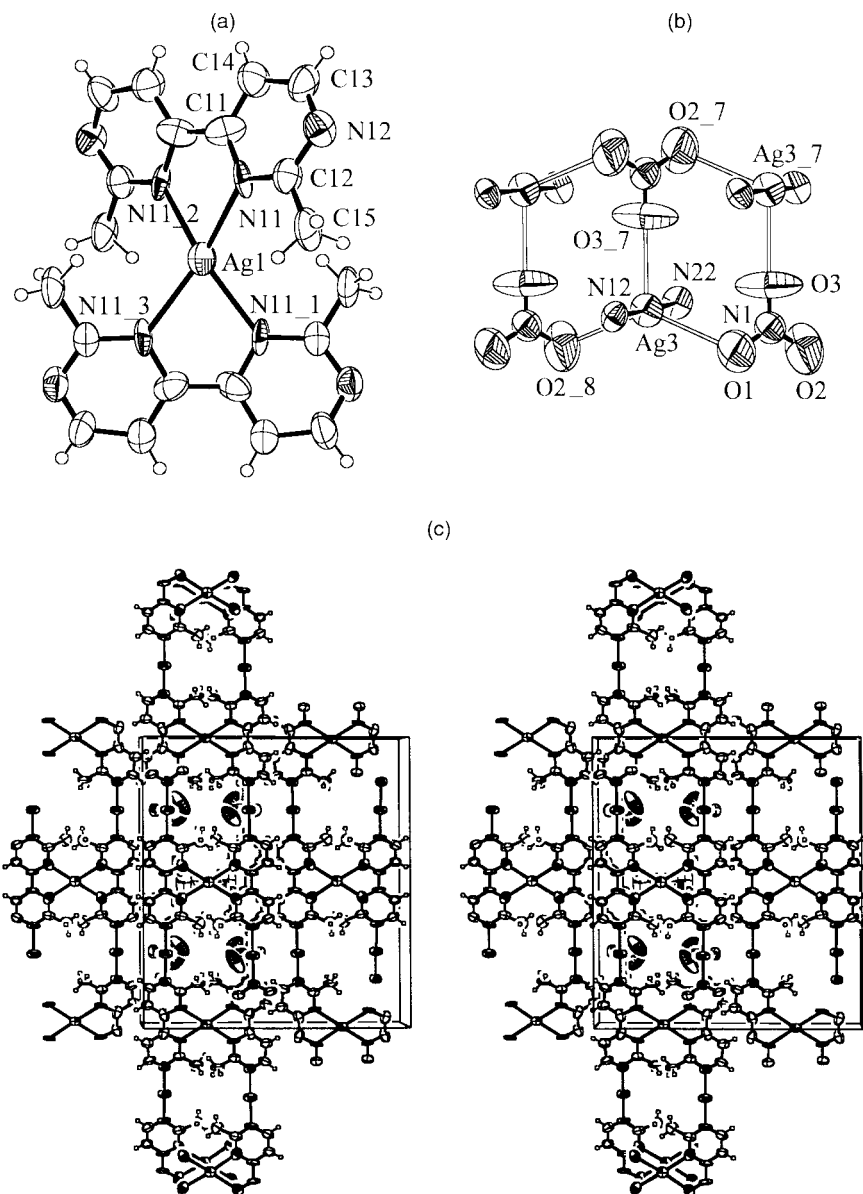


Fig. 7 (a) Sections of the co-ordination polymer of ${}^3_2[\text{Ag}_3(\mu_3\text{-NO}_3)_3(\mu_3\text{-L})_2]$ **10** showing one of the two bis-chelated silver centers. (b) Section of **10** which details the bridging action of Ag3 between the bis-chelate tectons of Ag1 and Ag2. Only the *exo*-dentate nitrogen donor atoms are shown for clarity. Also indicated is the connection of three silver atoms by a nitrate group and the surrounding of each Ag3 center by three nitrate ligands in the equatorial plane of the trigonal bipyramid. (c) Stereoscopic view along *a*. Selected distances [Å] and angles [°]: Ag(1)–N(11) 2.40(1), Ag(3)–N(22) 2.21(1), Ag(3)–N(12) 2.23(1), Ag(3)–O(1) 2.91(1), Ag(3)–O(2)_8 2.87(1) and Ag(3)–O(3)_7 2.78(1); N(11)_1–Ag(1)–N(11)_2 150.3(6), N(11)_1–Ag(1)–N(11)_3 116.1(5), N(11)_2–Ag(1)–N(11)_3 72.1(5), N(11)–Ag(1)–N(11)_3 150.3(6), N(12)–Ag(3)–N(22) 178.5(4), O(1)–Ag(3)–O(2)_8 134.3(5), O(1)–Ag(3)–O(3)_7 112.8(5) and O(2)_8–Ag(3)–O(3)_7 112.9(5). For the bis-chelated silver center Ag2 (similar to Ag1), which is not shown here: Ag(2)–N(21) 2.43(1), N(21)_4–Ag(2)–N(21)_5 148.7(7) and N(21)–Ag(2)–N(21)_6 117.2(6) (symmetry equivalent positions ${}_1 -x + \frac{1}{2}, y, -z + \frac{1}{2}$; ${}_2 -x + \frac{1}{2}, -y, z$; ${}_3: x, -y, -z + \frac{1}{2}$; ${}_4 -x + \frac{1}{2}, -y + 1, z$; ${}_5 x, -y + 1, -z + \frac{1}{2}$; ${}_6 -x + \frac{1}{2}, -y + 1, z$; ${}_7 x + \frac{1}{2}, y, -z$; ${}_8 x + 1, y, z$).

conditions allow one to steer between bidentate chelating or bridging. The case of silver(I) illustrates the effect of the anion and the metal-to-ligand ratio. The combination of both factors allows for the choice between bidentate bridging or tetradentate.

Depending on one's viewpoint the above results may be viewed as a hopeful step towards a certain understanding or as a still disappointing high number of variables. We acknowledge a high number of variables and do not pretend that we have reached a full understanding. With respect to the title of the manuscript, the individual reader according to his expectations may say if a sense of understanding has been reached. Structure-variable relations are not always as simple as we would like to have them. Yet, we feel that we could pinpoint certain correlations which should be taken into account in structure design. In co-ordination or crystal engineering we are likely to see a higher degree of complexity as we turn to multi-

dentate ligands or multicomponent metal-ligand systems. For this, it will be useful to develop a deeper understanding for the structure control through such factors as type of metal, the counter ion, the metal-to-ligand ratio and others. Within the concept of an "inorganic supramolecular library"¹² we plan eventually to be able to choose in an assembly or crystallization process those conditions which most likely lead to the target structural motif.

Experimental

The NMR spectra were collected on a Bruker ARX 200 (200.1 MHz for ${}^1\text{H}$, 50.3 MHz for ${}^{13}\text{C}$) or a Varian O-300 instrument (300.0 MHz for ${}^1\text{H}$, 75.4 MHz for ${}^{13}\text{C}$) and calibrated against the solvent signal (d_6 -DMSO, ${}^1\text{H}$ δ 2.53, ${}^{13}\text{C}$ δ 39.5), IR spectra on a Perkin-Elmer 783 spectrophotometer as KBr disks or Nujol mulls. Elemental analyses were carried out with a

Perkin-Elmer Elemental Analyzer E 240 C. X-Ray powder diffractograms (SUP 57608) were obtained with a Siemens powder diffractometer D5000 using Cu-K α radiation. All crystallizations of the silver complexes were carried out in the dark. The reactions with copper(I) iodide were carried out with Schlenk techniques using flame-dried glassware and argon as inert gas. Acetonitrile was dried by refluxing for 2 d over CaH₂ followed by distillation and storage under inert gas.

Preparations

2,2'-Dimethyl-4,4'-bipyrimidine L. To a solution of sodium (14 g, 0.61 mol) in dry ethanol (300 ml) was added under argon acetamidinium hydrochloride (56 g, 0.59 mol) at 0 °C. The pale yellow solution was stirred for 1 h, cooled to

-10 °C and then 1,6-bis(ethoxy)hexa-1,5-diene-3,4-dione¹³ (39.6 g, 0.20 mol) in dry ethanol (100 ml) was added dropwise. After complete addition, stirring was continued for 1 h at -10 °C, then the solution was allowed to warm to room temperature and stirred for 4 d. The solvent was removed in vacuum and the residue suspended in acetone (600 ml). The red-brown solid was filtered off, sublimed in vacuum and recrystallized from ethanol to give 16 g (42%) of colorless needles, mp 134–135 °C (lit. 133–135 °C¹³), bp. 229 °C (from DTA/TG). ¹H NMR (d₆-DMSO): δ 2.71 (s, 6 H, CH₃,CH₃'), 8.13 (dd, 2 H, *J* = 0.5, 5.0, H5,5') and 8.90 (d, 2 H, *J* = 5.0 Hz, H6,6'). ¹³C NMR (d₆-DMSO): δ 26.1 (CH₃,CH₃'), 114.6 (C5,5'), 158.5 (C4,4'), 161.1 (C2,2') and 168.3 (C6,6'). IR: 3060w, 2980w, 2950w, 1575s, 1545s, 1445s, 1390s, 1357s, 1185m, 1140w, 1100w, 1050m, 1000m, 840s, 770s, 655s, 588s, 427w and 404s cm⁻¹.

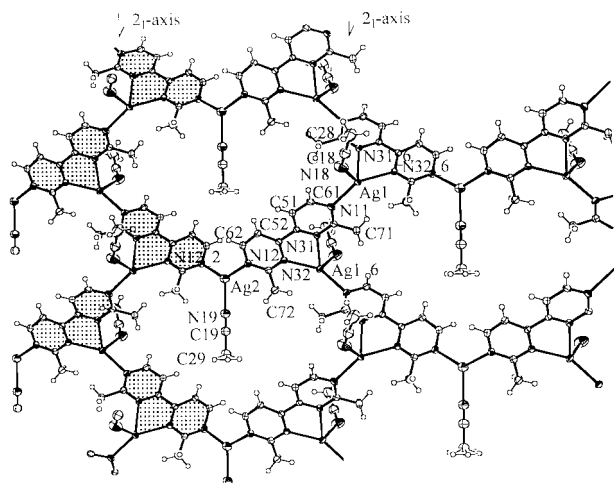


Fig. 8 Section of the two-dimensional co-ordination polymeric network of isostructural $\frac{2}{3}[\text{Ag}_3(\text{CH}_3\text{CN})_3(\mu_3\text{-L})_2][\text{BF}_4]_3$ **11** and $\frac{2}{3}[\text{Ag}_3(\text{CH}_3\text{CN})_3(\mu_3\text{-L})_2][\text{PF}_6]_3$ **12**, viewed along *a*. The acetonitrile ligand which points in the framework opening lies on a twofold axis; the hydrogen atoms are thus disordered. The BF₄⁻ and PF₆⁻ anions were omitted for clarity. One of the helicoidal one-dimensional substructures is highlighted by shading the bipyrimidine ligands. Selected distances [Å] and angles [°] for **11** [**12**]: Ag(1)–N(11) 2.229(2) [2.248(2)], Ag(1)–N(31) 2.383(2) [2.391(2)], Ag(1)–N(32) 2.301(2) [2.312(2)], Ag(1)–N(18) 2.442(3) [2.406(3)], Ag(2)–N(19) 2.272(4) [2.240(4)] and Ag(2)–N(12) 2.279(2) [2.278(2)]; N(11)–Ag(1)–N(32) 6 148.71(8) [143.30(6)], N(11)–Ag(1)–N(31) 6 126.59(7) [126.05(7)], N(31) 6–Ag(1)–N(32) 6 71.51(7) [71.58(6)], N(11)–Ag(1)–N(18) 93.49(9) [98.81(9)], N(32) 6–Ag(1)–N(18) 111.25(10) [110.47(9)], N(31) 6–Ag(1)–N(18) 95.45(10) [99.07(8)], N(19)–Ag(2)–N(12) 114.98(5) [114.65(5)] and N(12)–Ag(2)–N(12) 2 130.05(11) [130.7(1)] (symmetry equivalent positions $\frac{1}{2} - 2x - \frac{1}{2}, y, -z + 1$; $\frac{1}{2} - 6 - x, y + \frac{1}{2}, -z + \frac{1}{2}$).

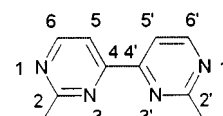


Fig. 9 Stereoscopic view of the two-dimensional co-ordination polymeric network of complexes **11** and **12**, viewed along *c* to show the folding of the layers and the helicoidal nature of the Ag1–ligand ribbon substructure (see text). Two BF₄⁻ anions (for **11**), one of them disordered, are included in the picture. Similarly, one of the PF₆⁻ anions in **12** is twofold disordered. The disordered BF₄⁻ or PF₆⁻ moiety is located inside a hydrophobic channel without well defined bonding sites for an anion.

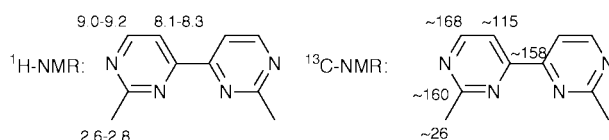
[Ni₃Cl₆(1)₂] 3. The ligand L (186 mg, 1.00 mmol) was dissolved in warm ethanol (40 ml) and added to a solution of NiCl₂·6H₂O (357 mg, 1.5 mmol) in dry ethanol (40 ml). After several days at room temperature a yellow precipitate had formed, which was filtered off, washed with a little ice-cold ethanol and dried for 5 min in vacuum. Yield 316 mg (83%). Further analytical data are in Table 1. The diffusion technique did not produce single crystals here, even when under rather dilute conditions. Compound **3** was slightly soluble in hot nitromethane and slow cooling gave crystals of **4**.

Aquadichloro(2,2'-dimethyl-4,4'-bipyrimidine)nickel(II)–nitromethane adduct, [NiCl₂(L)(H₂O)]·CH₃NO₂ 4. The ligand L (186 mg, 1.00 mmol) was dissolved in warm CH₃NO₂ (50 ml). To this solution was added NiCl₂·6H₂O (238 mg, 1.00 mmol) and the mixture heated to reflux for 5 min. The solution turned red and was filtered hot from the yellow precipitate, which by IR was shown to be complex **3**. The hot filtrate was slowly cooled to room temperature and within 3 d transparent light green rhombohedral platelets formed. Upon prolonged drying in air the crystals lose solvent of crystallization. The pink solution could be used for another extraction of the yellow precipitate to yield additional crystal batches. Each crystallization afforded 20 mg (5%) of product. A thermogravimetric analysis showed the loss of CH₃NO₂ at 77 °C and

Table 1 Elemental analyses, NMR and IR spectroscopic data of the metal complexes of L^a

Complex	Calc., Found (%)			¹ H NMR (d ₆ -DMSO) ^b , δ(J/Hz)-	¹³ C NMR (d ₆ -DMSO) ^b , δ	IR (KBr, cm ⁻¹) ^c
	C	H	N			
3 [Ni ₃ Cl ₆ (L) ₂]	31.56 31.83	2.65 2.65	14.72 14.76	2.58 (s), 8.12 (s), 9.12 (s, br)	23.9, 113.3, 156.1, 158.1, 166.7	3400m (br), 3065m, 1603s, 1570s, 1560s, 1470s, 1450s, 1410m, 1395m, 1155s, 1040m, 880m, 865s, 767m, 745m, 670m, 595w
4 [NiCl ₂ (L)(H ₂ O)]· CH ₃ NO ₂	33.46 33.10	3.83 3.69	17.74 17.25	2.60 (s), 4.30 (s, H ₂ O), 8.12 (s), 9.18 (s, br)		3400m (br), 1613s, 1600s, 1590s, 1557s, 1547s, 1457s, 1406s, 1377m, 1201m, 1149m, 1110m, 875m, 855s, 757s, 740m, 660s, 595m
5 ¹ / ₂ [Cu(NO ₃) ₂ · (μ-L)]	32.14 32.15	2.67 2.67	22.44 22.48	2.61 (s, br), 8.18 (s, br), 9.18 (s, br)		1601m, 1578w, 1510m, 1458m, 1390s, 1294m, 1270m, 1022m, 873w, 811w, 760w, 688m, 599w
6 [Cu ₃ I ₃ (L)]	15.86 15.96	1.33 1.29	7.40 7.40			1580s, 1550m, 1445s, 1392m, 1155m, 843s, 750s, 661s, 595w
7 ² / ₃ [Cu ₂ (μ ₃ -I) ₂ · (μ-L)]	21.18 21.07	1.76 1.72	9.88 9.84			1580s, 1534s, 1433s, 1410m, 1350m, 1269m, 1190m, 1100m, 1038m, 1010s, 755s, 660s, 590w, 410m
8 ¹ / ₂ [Cu(μ-I)(L)]	31.89 31.78	2.68 3.53	14.88 17.65			1582s, 1560s, 1550s, 1447s, 1398m, 1320m, 1190m, 1145m, 1110m, 835s, 760s, 649s, 588m, 424s
9 ² / ₃ [Ag(μ-NO ₃)· (μ-L)]	33.73 33.75	2.83 2.71	19.67 19.67	2.80 (s), 8.30 (dd, J = 5.1, 0.5), 9.01 (d, J = 5.1)	26.4, 115.4, 159.1, 159.9, 167.8	1580s, 1540s, 1434s, 1410s, 1390s, 1316s, 1275s, 1190m, 1037m, 850s, 830w, 820m, 760m, 660s, 588w, 410m
10 ³ / ₂ [Ag ₃ (μ ₃ -NO ₃) ₃ (μ ₃ -L)]	17.64 17.32	2.28 2.56	17.47 17.18	2.81 (s), 8.12 (dd, J = 5.1, 0.5), 9.03 (d, J = 5.1)	26.6, 115.7, 158.7, 160.1, 167.8	1770m, 1580s, 1540s, 1440s, 1390s (br), 1275m, 1190m, 1100m, 1040m, 1010m, 853s, 830s, 762s, 662s, 593m, 410s
11 ² / ₃ [Ag ₃ (CH ₃ CN) ₃ (μ ₃ -L) ₂][BF ₄] ₃	28.92 28.05	2.71 2.60	14.27 13.84			1579s, 1569s, 1538s, 1435s, 1137s, 1087s, 1036s, 1006m, 850m, 833m, 758m, 658m, 649m, 583w, 538m, 525m
12 ² / ₃ [Ag ₃ (CH ₃ CN) ₃ (μ ₃ -L) ₂][PF ₆] ₃	24.90 24.88	2.33 1.96	12.29 12.60			1580s, 1570s, 1540s, 1435s, 1385m, 1352m, 850vs, 832s, 760m, 740w, 658w, 650w, 565s

^a Color, yield and thermal behavior are described in the individual preparative procedures. ^b The peak assignment is as given for free 2,2'-dimethyl-4,4'-bipyrimidine:



^c Mostly medium and stronger IR frequencies reported, only.

of one third of the bipyrimidine ligands at 231 °C, possibly to yield **3**.

(μ-2,2'-Dimethyl-4,4'-bipyrimidine)dinitratocopper(II), ¹/₂[Cu(NO₃)₂(μ-L)] **5**. A solution of L (186 mg, 1.00 mmol) in CHCl₃ (10 ml) was overlaid in a test-tube first with CH₂Cl₂ (2 ml) and then with a solution of Cu(NO₃)₂·6H₂O (296 mg, 1.00 mmol) in ethanol (5 ml). Within several hours the contact area of the solutions turned red and after 2 weeks deep blue-violet crystals began to grow within the red zone. After 2 months a homogeneous red solution had formed with crystals at the bottom of the test-tube. They were collected, washed with a little ice-cold ethanol and air-dried. The yield could be increased by concentrating the mother-liquor; 307 mg (82%). A thermogravimetric analysis showed an exothermic decomposition at 198 °C to volatile components and CuO. The crystal composition did not depend on the concentrations employed or on the metal-to-ligand ratio. The latter was varied from 10:1 to 1:10.

[Cu₃I₃(L)] 6. A 50 ml Schlenk tube was filled with water-free CuI (571 mg, 3.0 mmol), followed by dry CH₃CN (10 ml). The solution was then carefully overlaid with a solution of L (186 mg, 1.0 mmol) in dry CH₃CN (20 ml). A fine black precipitate occurred immediately. Within 3 d CuI was completely transformed into strongly intergrown needle-shaped crystals. These were separated by filtration, washed with a few ml of acetonitrile and dried for 5 min in vacuum. Yield 705 mg (93%). A thermogravimetric analysis indicated the loss of L

and the transformation into CuI at 336 °C. When stored in the mother-liquor, the black needles of complex **6** started to turn into bright red cubes of **7** within a few days. When the black-red needles of **6** were heated in dimethyl sulfoxide, the compound could be transformed into the co-ordination polymer **8**.

(μ-2,2'-Dimethyl-4,4'-bipyrimidine)di(μ₃-iodo)dicopper(I), ²/₃[Cu₂(μ₃-I)₂(μ-L)] **7**. Copper(I) iodide (391 mg, 2.0 mmol) in CH₃CN (10 ml) and a solution of L (186 mg, 1.0 mmol) in acetonitrile (20 ml) gave a black precipitate of complex **6** which was kept under the mother-liquor. After 2 to 3 weeks cubic red crystals had grown which were separated from some of the remaining black precipitate by suspension and decantation. The product was dried for 5 min in vacuum. Yield 442 mg (78%). A thermogravimetric analysis showed the loss of one third of the bipyrimidine ligands at 273 °C, possibly yielding **6**, followed by the complete loss of L at 334 °C to give CuI.

(2,2'-Dimethyl-4,4'-bipyrimidine)(μ-iodo)copper(I), ¹/₂[Cu(μ-I)(L)] **8**. Compound **6** (126 mg, 0.167 mmol) was dissolved in DMSO (100 ml) upon heating. Starting from 120 °C the solution was cooled to room temperature at a rate of 2 °C h⁻¹. The deep red, metallic lustrous needles were filtered off, washed with a little DMSO and dried in vacuum for 15 min. Yield 51 mg (81%). The needles appeared black metallic under the microscope when their thickness extended over 20 μm.

Regardless of the metal-to-ligand ratio, complex **6** was always obtained as the first phase in the synthesis of **7** and **8**.

Table 2 Crystal data for compounds 4, 5, 7–12

	4	5	7	8	9	10	11	12
Formula	$C_{11}H_{15}Cl_2N_5NiO_3$	$C_{10}H_{10}CuN_6O_6$	$C_{10}H_{10}Cu_2I_2N_4$	$C_{10}H_{10}CuN_4$	$C_{10}H_{10}AgNO_3$	$C_{20}H_{20}Ag_3N_{11}O_9$	$C_{26}H_{29}Ag_3B_3F_{12}N_{11}$	$C_{26}H_{29}Ag_3F_{18}N_{11}P_3$
<i>M</i>	406.88	373.78	567.10	376.66	356.09	882.08	1079.60	1254.08
<i>T/K</i>	200(2)	294(2)	200(2)	293(2)	200(3)	293(2)	200(3)	200(3)
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Fdd2$	$Pbcn$	<i>Pena</i>	<i>I2/a</i>	<i>I2/a</i>
<i>a/Å</i>	13.506(3)	6.111(8)	7.751(1)	33.436(2)	3.822(5)	7.068(8)	17.1706(11)	17.3846(11)
<i>b/Å</i>	7.6665(10)	7.445(8)	10.5927(8)	35.0765(18)	15.405(5)	21.81(2)	10.8107(7)	10.9689(10)
<i>c/Å</i>	15.374(3)	9.335(8)	4.2001(7)	4.0449(2)	19.739(5)	19.41(2)	21.3415(13)	21.9716(14)
α°	100.69(2)	82.29(8)	91.81(2)					
β°		83.07(8)	101.99(2)					
γ°		67.23(8)	88.54(2)					
<i>V/Å³</i>	1564.3(5)	387.0(7)	337.1(1)	4747.8(4)	1162.2(16)	2992(5)	3729.7(4)	4044.2(5)
<i>Z</i>	4			16	4	4	4	4
<i>D/g cm⁻³</i>	1.668	1.604	2.794	2.108	2.035	1.958	1.923	2.060
μ/cm^{-1}	15.98	14.51	77.19	44.18	18.10	20.09	16.58	16.78
Measured reflections	9078	2009	3494	10123	5798	3483	21256	17161
Unique reflections (<i>R_{int}</i>)	3507 (0.0685)	1759 (0.0677)	1492 (0.0343)	2811 (0.0405)	1336 (0.0381)	3453	4440 (0.0412)	4568 (0.0524)
Parameters refined	248	107	97	163	108	212	275	284
Maximum, minimum $\Delta\rho/e \text{ \AA}^{-3}$	0.0890; -0.968	0.943; -1.302	1.601; -0.714	1.179; -0.327	0.485; -0.709	1.295; -1.759	0.963; -0.670	1.001; -0.964
<i>R</i> 1; <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0409; 0.0985	0.0726; 0.1784	0.0231; 0.0544	0.0215; 0.0494	0.0236; 0.0559	0.0973; 0.2336	0.0291; 0.0755	0.0364; 0.0974
all reflections	0.0552; 0.1042	0.0899; 0.2087	0.0265; 0.0553	0.0239; 0.0501	0.0345; 0.0586	0.2154; 0.3477	0.0325; 0.0771	0.0403; 0.0996

An X-ray powder diffraction study showed that **6** was different from both **7** and **8**.

(μ -2,2'-Dimethyl-4,4'-bipyrimidine)(μ -nitrate)silver(I), $[\text{Ag}(\mu\text{-NO}_3)(\mu\text{-L})]$ **9**. A solution of **L** (186 mg, 1.0 mmol) in CHCl_3 (10 ml) was overlaid with a solution of AgNO_3 (170 mg, 1.0 mmol) in water (10 ml) in a crystallization dish. The reaction mixture was stored in the dark. Within a few hours colorless crystals started to grow at the phase boundary. When the organic chloroform solvent had evaporated the crystals were collected by filtration, washed with some water and ethanol and dried in air. They were of needle shape but intergrown to bushels and had a mother-of-pearl like shine. Yield 324 mg (91%). A thermogravimetric analysis showed loss of 50% of the bipyrimidine ligands at 239 °C and at 273 °C an exothermic decomposition to volatile products and Ag_2O .

Bis(μ_3 -2,2'-dimethyl-4,4'-bipyrimidine)tri(μ_3 -nitrate)-trisilver(I), $[\text{Ag}_3(\mu_3\text{-NO}_3)_3(\mu_3\text{-L})_2]$ **10**. A solution of **L** (112 mg, 0.60 mmol) in CHCl_3 (6 ml) was overlaid in a test tube first with CH_2Cl_2 (2 ml) and then with a solution of AgNO_3 (225 mg, 1.50 mmol) in water (6 ml). Within 12 h yellow crystals formed at the phase boundary. The crystals were collected, washed with a few milliliters of water and air-dried. Preparation and storage was mostly carried out in the dark. Yield 217 mg (88%). A thermogravimetric analysis indicated decomposition to Ag_2O and volatile oxidation products at 272 °C.

Tris(acetonitrile)bis(μ_3 -2,2'-dimethyl-4,4'-bipyrimidine)-trisilver tris(tetrafluoroborate), $[\text{Ag}_3(\text{CH}_3\text{CN})_3(\mu_3\text{-L})_2][\text{BF}_4]_3$ **11**. A solution of **L** (9 mg, 0.05 mmol) in CH_2Cl_2 (5 ml) was overlaid in a test-tube with a solution of AgBF_4 (10 mg, 0.05 mmol) in ethanol (5 ml). After 8 d at room temperature the yellow crystals formed were collected, washed with water and dichloromethane and dried under vacuum. Yield 9 mg (47%). According to IR spectroscopy the same complex was also obtained from a metal-to-ligand ratio of 2:1.

Tris(acetonitrile)bis(μ_3 -2,2'-dimethyl-4,4'-bipyrimidine)-trisilver tris(hexafluorophosphate), $[\text{Ag}_3(\text{CH}_3\text{CN})_3(\mu_3\text{-L})_2][\text{PF}_6]_3$ **12**. A solution of **L** (9 mg, 0.05 mmol) in CH_2Cl_2 (5 ml) was overlaid in a test-tube with a solution of AgPF_6 (27 mg, 0.11 mmol) in ethanol (5 ml). After 8 d at room temperature the yellow crystals formed were collected, washed with water and dichloromethane and dried under vacuum. Yield 13 mg (50%).

Crystal structure determinations

Data were collected with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and the use of a graphite monochromator. Structure solution was performed by direct methods using SHELXS 97 or SHELXS 86³⁷ except for complexes **7** and **8** where SIR 97³⁸ was employed. Refinement: full-matrix least squares on F^2 [SHELXL 97 (version 97-2), SHELXS 93];³⁷ non-hydrogen positions found and refined with anisotropic thermal parameters. Crystal data are listed in Table 2. Compound **8** was refined as a racemic twin. Graphics were computed with ORTEP 3 for Windows.³⁹

CCDC reference number 186/1560.

See <http://www.rsc.org/suppdata/dt/1999/3121/> for crystallographic files in .cif format.

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