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

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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 [NiL(H₂O)]·CH₃NO₂ derived from hot CH₃NO₂. With Cu(NO₃)₂ and CuL·CH₃CN one- and two-dimensional (1-D and 2-D) co-ordination polymers of formula [Cu(NO₃)₂(μ-L)] and [Cu(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 CuL and crystallization from hot dimethyl sulfoxide leads to a 1-D iodide-bridged co-ordination polymer [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, [Ag(μ-NO₃)(μ-L)], with only bridging bipyrimidine ligands is observed. At a metal excess, a 3-D framework, [Ag₃(μ₃-NO₃)(μ₄-L)], 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 PF₅⁻, and gives rise to the isotypical 2-D co-ordination polymers of formula [Ag₆(CH₃CN)₉(μ₄-L)]X₉ (X = BF₄ or PF₅).

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

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


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 polymers based on the endo-chelation of two ligands with an appropriate metal center (I) 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-naphthylidine⁷ or 5,5′-dicyano-2,2′-bipyridine⁸ and ligands of the tris(pyrazolyl)borate type for the assembly of metal co-ordination polymers.⁹ In this paper the ligand 2,2′-dimethyl-4,4′-bipyrimidine (L) serves as an example to derive at 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.¹⁰ While rigid bidentate ligands, for example, allow only for one result in the metal co-ordination process, flexible and multidentate ligands...
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. 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. 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 ring. A semiempirical PM3 calculation in vacuum and in chloroform supported the assignment of the s-trans form as the preferred conformation.

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 coordination modes of the ambidentate bipyrimidine ligand: bidentate chelating, bidentate bridging, tridentate, and tetradoentate. The tridentate mode has been observed before, 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 determinator 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, [NiCl2-(L)(H2O)]CH3NO2). Copper(ii) was only found in the bidentate bridging mode (5, [Cu(NO3)2(μ-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, [Cu(µ-I)(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, [Cu(µ-I)(μ-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 CH3NO2. 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 calculation 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. 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.

A tridentate co-ordination mode of copper(i) with L was described earlier in the compound [Cu4(CH3CN)2(μ-L)][PF6]6. There, the participation of one exo- and both endo-nitrogen donors yields an infinite helicoidal polymeric chain around a 2, 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.
Then one derives the structure of 9, \([\text{Ag}\{\mu-\text{NO}_3\}\{\mu-L\}]\), with solely bridging co-ordination. Otherwise, if an excess of silver was used in the case of the \(\text{NO}_3\) anion, tetradeptate co-ordination was achieved. The structure of 10, \([\text{Ag}_3\{\mu_3-\text{NO}_3\}_3\{\mu_3-L\}_2]\), 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"-coordinating counter ions \(\text{BF}_4^-\) and \(\text{PF}_6^-\) were employed as their silver salts as starting materials. The crystalline products 11 and 12, \([\text{Ag}_3\{\text{CH}_3\text{CN}\}_3\{\mu_3-L\}_2\}X_3\), from \(\text{AgBF}_4\) and \(\text{AgPF}_6\), respectively, were found to be isostructural.\(^{19,20}\) The structures exhibit the tetradeptate co-ordination mode. The result did not depend on the metal-to-ligand ratio here, which was 1:1 in the case of \(X = \text{BF}_4^-\) (11) and 2:1 for \(X = \text{PF}_6^-\) (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 tetradeptate chelating/bridging ligands. The individual structures are briefly described in more detail in the following.

\[\text{NiCl}_2(L)(H_2O)\] 4. Fig. 2 illustrates the molecular structure of aquadichloro(2,2'-dimethyl-4,4'-bipyrimidine)-nickel(II): a chelate complex with \(s\text{-cis}\) conformation of the pyrimidine rings. A somewhat unusual trigonal-bipyramidal geometry around nickel(II) is found,\(^2\) 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 octachiral co-ordination polyhedron. A nitromethane molecule is incorporated in the lattice but with distances larger than 3 Å from the metal atom.

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(II) (b) and silver(II) (c).
is a distorted tetrahedron. The bipyrimidine ligands have a role and two iodine atoms. The co-ordination polyhedron at copper 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 of a spacer between the stairs and bridge the strands to a layer structure.

Fig. 4 Layer structure of the two-dimensional co-ordination polymer $[\text{Cu}_2(\mu-I)_3(\mu-L)]_n$ 7 with an infinite one-dimensional Cul substructure bridged by bipyrimidine ligands, viewed perpendicular to the $ab$ plane. Selected distances [$\AA$] and angles [$^\circ$]: Cu-I 2.601(7), Cu-I 4 2.6532(7), Cu-I 2.7347(8), Cu-N(1) 2.030(3), Cu$\cdots$Cu 4 2.649(1), Cu-I-Cu 4 60.53(2), Cu 3-I-Cu 4 103.80(2), Cu-I 4-Cu 3 82.61(2), N(1)-Cu-I 113.3(1), N(1)-Cu-I 114.5(1), Ni(1)-Cu-I 105.03(9), I-Cu-I 4 119.47(2), I-Cu-I 113.80(2) and I-Cu-I 4 97.39(2) (symmetry equivalent positions $x$, $y$, $z$; $-x+1$, $-y+1$, $-z+1$).

Fig. 5 Chain structure along $c$ of the one-dimensional co-ordination polymer $[\text{Cu}(\mu-I)L]_n$ 8 with a Cul zig zag chain substructure. Selected distances [$\AA$] and angles [$^\circ$]: Cu-I 2.5374(5), Cu-I 1 2.5937(5), Cu-N(13) 2.091(2) and Cu-N(23) 2.079(2), Cu-I 1-Cu-I 1-Cu-I 1 104.09(14), N(13)-Cu-N(23) 79.45(10), N(13)-Cu-I 127.00(8), N(13)-Cu-I 104.84(8), N(23)-Cu-I 122.05(10) and N(23)-Cu-I 1 118.27(10) (symmetry equivalent position: $x$, $y$, $z$).

Fig. 6 The structure of the three-dimensional network of complex 9. The framework can be thought of being built up from zig zag Ag$\cdots$Ag$\cdots$Ag$\cdots$NO$_3$ 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.

Fig. 7 The structure of the three-dimensional framework of complex 10 is shown in Fig. 7.
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 nitroate 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.

\[ \text{Ag}_2(\text{CH}_3\text{CN})(\mu_2-\text{L})_2 \text{X}_2 \text{with } X = \text{BF}_4 (11) \text{ or PF}_6 (12) \]

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 nitroate donors of a chelating bipyrimidine ligand, an exo-nitroate donor of a bridging group and an acetonitrile molecule. The environment of Ag2 is three-co-ordinated and made up of two exo-dentate nitroate donor atoms from bridging bipyrimidine ligands and a \( \text{CH}_3\text{CN} \) molecule. In a different perspective, the structures of 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, 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 \( \text{Ni}^{2+} \) and \( \text{Cu}^{2+} \) 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
Conditions allow one to steer between bidentate chelating or bridging. The case of silver(1) 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 tetra-dentate.

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. Within the concept of an "inorganic supramolecular library" 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 1H, 50.3 MHz for 13C) or a Varian O-300 instrument (300.0 MHz for 1H, 75.4 MHz for 13C) and calibrated against the solvent signal of DMSO. 1H δ 2.53, 13C 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-Kα 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-dione¹⁹ (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 °C), bp 229 °C (from DTA/TG). ¹H NMR (d₆-DMSO): δ 2.71 (s, 6 H, CH₃CH₂), 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 (CH₃CH₂), 114.6 (C5,5'), 158.5 (C4,4'), 161.1 (C2,2') and 168.3 (C6,6'). IR: 3060w, 2920w, 2950s, 1575s, 1545s, 1445s, 1390s, 1357s, 1185m, 1140w, 1100w, 1050m, 1000m, 840s, 770s, 588s, 427w and 404s cm⁻¹.

Fig. 8 Section of the two-dimensional co-ordination polymeric network of isostructural [Ag₂(CH₃CN)₂(L)₂][BF₄]·₆H₂O 11 and [Ag₂(CH₃CN)₂(L)₂][PF₆]·₆H₂O 12, viewed along a. The acetonitrile ligand which points in the framework opening lies on an 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 and angles [Å] and [°] 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) 2.620(2) [2.312(2), Ag(1)–N(18) 2.442(3) [2.406(3), Ag(1)–N(19) 2.278(4) [2.248(4)] and Ag(2)–N(11) 2.279(2) [2.278(2), N(11)–Ag(1)–N(32) 148.7(1) [143.30(6), N(11)–Ag(1)–N(31) 126.5(9) [126.05(7)], N(31)–6–Ag(1)–N(32) 6 134.3(10) [99.07(6), N(19)–Ag(2)–N(12) 117.4(5) [114.65(5), N(12)–Ag(2)–N(11) 130.0(5) [130.71] (symmetry equivalent positions 2–x = ½, y, z–1; 6–x, y + ½, z–½).

Ni₃Cl₆(L)_2ClO₄. 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. 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
of one third of the bipyrimidine ligands at 231 °C, possibly to yield 3.

\((\text{Cu}(\text{NO}_3)_3)_2(\text{dmt})\) 5. A solution of L (186 mg, 1.00 mmol) in CHCl₃ (10 ml) was overlayered in a test-tube first with CH₂Cl₂ (2 ml) and then with a solution of Cu(NO₃)₂·3H₂O (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.

\([\text{CuL}_2]\) 6. A 50 ml Schlenk tube was filled with water-free CuI (571 mg, 3.0 mmol), followed by dry CH₂CN (10 ml). The solution was then carefully overlaid with a solution of L (186 mg, 1.0 mmol) in dry CH₂CN (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 cubics 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.

\((\text{Cu}(\text{NO}_3)_3)_2(\text{dmt})\) 7. Copper(i) iodide (391 mg, 2.0 mmol) in CH₂CN (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.

\((\text{Cu}(\text{NO}_3)_3)_2(\text{dmt})\) 8. Compound 6 (126 mg, 0.167 mmol) was dissolved in DMSO (100 ml) under 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.

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**Table 1**  Elemental analyses, NMR and IR spectroscopic data of the metal complexes of L⁻

<table>
<thead>
<tr>
<th>Complex</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>¹H NMR (d₂-DMSO)(^α), δ (Hz)</th>
<th>¹C NMR (d₂-DMSO)(^α), δ</th>
<th>IR (KBr, cm⁻¹)(^α)</th>
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</thead>
<tbody>
<tr>
<td>3 ([\text{NiCl}_2(\text{L})_2])</td>
<td>31.56</td>
<td>2.65</td>
<td>14.72</td>
<td>2.58 (s), 8.12 (s), 9.12 (s, br)</td>
<td>23.9, 113.3, 156.1, 158.1, 166.7</td>
<td>3400 (br), 3065m, 1603s, 1570s, 1568s, 1470s, 1450s, 1410m, 1395m, 1155s, 1040m, 880m, 865s, 767m, 745m, 670m, 595w</td>
</tr>
<tr>
<td>4 ([\text{NiCl}_2(\text{L})(\text{H}_2\text{O})_2])</td>
<td>33.46</td>
<td>3.83</td>
<td>17.74</td>
<td>2.60 (s), 4.30 (s), 8.12 (s), 11.98 (s, br)</td>
<td>26.1 (s, br), 8.18 (s, br), 9.18 (s, br)</td>
<td>1601m, 1578w, 1501m, 1458m, 1390s, 1294m, 1270m, 1022m, 873m, 811m, 768w, 685s, 599w</td>
</tr>
<tr>
<td>5 ([\text{Cu}(\text{NO}_3)\text{Br}]_2(\text{L}))</td>
<td>32.14</td>
<td>2.67</td>
<td>22.44</td>
<td>2.61 (s, br), 8.18 (s, br), 9.18 (s, br)</td>
<td>1601m, 1578w, 1501m, 1458m, 1390s, 1294m, 1270m, 1022m, 873m, 811m, 768w, 685s, 599w</td>
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</tr>
<tr>
<td>6 ([\text{CuL}_2])</td>
<td>15.86</td>
<td>3.33</td>
<td>7.40</td>
<td>1580s, 1500m, 1445s, 1392m, 1155m, 843s, 750s, 661s, 599w</td>
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<td></td>
</tr>
<tr>
<td>7 ([\text{Cu}(\text{μ$_2$-L})_2])</td>
<td>21.18</td>
<td>1.76</td>
<td>9.88</td>
<td>1580s, 1534s, 1433s, 1410m, 1350m, 1269m, 1190m, 1100m, 1038m, 1010s, 755s, 660s, 590m, 410m</td>
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<td></td>
</tr>
<tr>
<td>8 ([\text{Cu}(\text{μ$_2$-L})_2])</td>
<td>31.89</td>
<td>2.68</td>
<td>14.88</td>
<td>1582s, 1560s, 1550s, 1447s, 1398m, 1320m, 1190m, 1145m, 1110m, 835s, 760s, 649s, 588m, 424s</td>
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<tr>
<td>9 ([\text{Ag}(\text{μ$_2$-NO$_3$})_2(\text{L})])</td>
<td>33.73</td>
<td>2.83</td>
<td>19.67</td>
<td>2.80 (s), 8.30 (d, J = 5.1, 0.5), 9.01 (d, J = 5.1)</td>
<td>1599, 167.4, 159.1, 159.2, 166.7</td>
<td>1580s, 1450s, 1343s, 1410s, 1390s, 1316s, 1275s, 1190m, 1037m, 850s, 820m, 760m, 660s, 588s, 410m</td>
</tr>
<tr>
<td>10 ([\text{Ag}(\text{μ$_2$-NO$_3$})_2(\text{L})])</td>
<td>17.64</td>
<td>2.28</td>
<td>17.47</td>
<td>2.81 (s), 8.12 (dd, J = 5.1, 0.5), 9.03 (d, J = 5.1)</td>
<td>1601, 157.7, 158.7, 161.0, 167.8</td>
<td>1770m, 1580s, 1540s, 1440s, 1390s (br), 1275m, 1190m, 1100m, 1040m, 1010m, 853s, 830s, 762s, 662s, 593m, 410s</td>
</tr>
<tr>
<td>11 ([\text{Ag}(\text{CHCN})_2(\text{μ$_2$-L})_2][\text{BF}_4]_2)</td>
<td>28.92</td>
<td>2.71</td>
<td>14.27</td>
<td>1579s, 1569s, 1538s, 1435s, 1137s, 1087s, 1036s, 1006m, 850m, 833m, 758m, 658m, 649m, 583s, 538m, 525m</td>
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<tr>
<td>12 ([\text{Ag}(\text{CHCN})_2(\text{μ$_2$-L})_2][\text{PF}_6]_2)</td>
<td>24.90</td>
<td>2.33</td>
<td>12.29</td>
<td>1580s, 1570s, 1540s, 1435s, 1385m, 1352m, 850s, 832s, 760m, 740w, 658s, 650w, 565s</td>
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</table>

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

\(^α\) Mostly medium and stronger IR frequencies reported, only.
Table 2  Crystal data for compounds 4, 5, 7–12

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>5</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
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<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₁₄H₁₂Cl₂NiNO₅</td>
<td>C₁₅H₁₉CuN₂O₆</td>
<td>C₁₅H₁₉Cu₂N₂</td>
<td>C₁₅H₁₉Cu₂N₄</td>
<td>C₁₅H₁₉Cu₂N₄</td>
<td>C₁₅H₁₉AuNO₃</td>
<td>C₁₅H₁₉Ag₂NiO₄</td>
<td>C₁₅H₁₉Ag₂B₃F₁₂N₁₁</td>
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<tr>
<td><strong>M</strong></td>
<td>406.88</td>
<td>373.78</td>
<td>567.10</td>
<td>376.66</td>
<td>356.09</td>
<td>882.08</td>
<td>1079.60</td>
<td>1254.08</td>
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<tr>
<td><strong>T/K</strong></td>
<td>200(2)</td>
<td>294(2)</td>
<td>200(2)</td>
<td>293(2)</td>
<td>200(3)</td>
<td>293(2)</td>
<td>200(3)</td>
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<tr>
<td><strong>Crystal system</strong></td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P2₁/n</td>
<td>P1</td>
<td>P1</td>
<td>Fd2</td>
<td>Pbn</td>
<td>Pna</td>
<td>P2a</td>
<td>P2a</td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td>13.50(6)</td>
<td>7.666(5)</td>
<td>15.37(4)</td>
<td>10.69(2)</td>
<td>7.75(1)</td>
<td>3.43(2)</td>
<td>3.82(5)</td>
<td>7.06(8)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>6.11(1)</td>
<td>7.44(8)</td>
<td>9.33(8)</td>
<td>8.22(8)</td>
<td>10.59(2)</td>
<td>3.33(2)</td>
<td>15.40(5)</td>
<td>17.10(6)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>7.666(5)</td>
<td>7.44(8)</td>
<td>9.33(8)</td>
<td>8.22(8)</td>
<td>10.59(2)</td>
<td>3.33(2)</td>
<td>15.40(5)</td>
<td>17.10(6)</td>
</tr>
<tr>
<td><strong>α/°</strong></td>
<td>13.50(6)</td>
<td>7.666(5)</td>
<td>15.37(4)</td>
<td>10.69(2)</td>
<td>7.75(1)</td>
<td>3.43(2)</td>
<td>3.82(5)</td>
<td>7.06(8)</td>
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<tr>
<td><strong>β/°</strong></td>
<td>7.666(5)</td>
<td>7.44(8)</td>
<td>9.33(8)</td>
<td>8.22(8)</td>
<td>10.59(2)</td>
<td>3.33(2)</td>
<td>15.40(5)</td>
<td>17.10(6)</td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
<td>7.666(5)</td>
<td>7.44(8)</td>
<td>9.33(8)</td>
<td>8.22(8)</td>
<td>10.59(2)</td>
<td>3.33(2)</td>
<td>15.40(5)</td>
<td>17.10(6)</td>
</tr>
<tr>
<td><strong>V/Å³</strong></td>
<td>1371(1)</td>
<td>1162.2(16)</td>
<td>337.1(1)</td>
<td>4747.8(4)</td>
<td>4292(5)</td>
<td>3729.7(4)</td>
<td>4044.2(5)</td>
<td>4044.2(5)</td>
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<tr>
<td><strong>Z</strong></td>
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<td>4</td>
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<td>4</td>
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<tr>
<td><strong>D/ρ cm⁻³</strong></td>
<td>1.668</td>
<td>1.604</td>
<td>2.794</td>
<td>2.108</td>
<td>2.035</td>
<td>1.958</td>
<td>1.923</td>
<td>2.060</td>
</tr>
<tr>
<td><strong>μ/cm⁻¹</strong></td>
<td>15.98</td>
<td>14.51</td>
<td>17.19</td>
<td>18.18</td>
<td>18.18</td>
<td>20.09</td>
<td>16.58</td>
<td>16.78</td>
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<tr>
<td><strong>Measured reflections</strong></td>
<td>9078</td>
<td>2009</td>
<td>3484</td>
<td>10123</td>
<td>5798</td>
<td>3483</td>
<td>21256</td>
<td>17161</td>
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<tr>
<td><strong>Unique reflections (Rint)</strong></td>
<td>3507 (0.0685)</td>
<td>1759 (0.0677)</td>
<td>1492 (0.0343)</td>
<td>2811 (0.0405)</td>
<td>1336 (0.0381)</td>
<td>3453</td>
<td>4440 (0.0412)</td>
<td>4568 (0.0524)</td>
</tr>
<tr>
<td><strong>Parameters refined</strong></td>
<td>248</td>
<td>107</td>
<td>97</td>
<td>163</td>
<td>108</td>
<td>212</td>
<td>275</td>
<td>284</td>
</tr>
<tr>
<td><strong>Maximum, minimum</strong></td>
<td>0.0890; -0.968</td>
<td>0.943; -1.302</td>
<td>1.601; -0.714</td>
<td>1.179; -0.327</td>
<td>0.485; -0.709</td>
<td>1.295; -1.759</td>
<td>0.963; -0.670</td>
<td>1.001; -0.964</td>
</tr>
<tr>
<td><strong>Δρ/ρ Å⁻³</strong></td>
<td>0.0409; 0.0985</td>
<td>0.0726; 0.1784</td>
<td>0.0231; 0.0544</td>
<td>0.0215; 0.0494</td>
<td>0.0236; 0.0559</td>
<td>0.0973; 0.2336</td>
<td>0.0291; 0.0755</td>
<td>0.0364; 0.0974</td>
</tr>
<tr>
<td><strong>R1 = R2 [I &gt; 2σ(I)]</strong></td>
<td>0.0552; 0.1042</td>
<td>0.0899; 0.2087</td>
<td>0.0265; 0.0553</td>
<td>0.0239; 0.0501</td>
<td>0.0045; 0.0586</td>
<td>0.2154; 0.3477</td>
<td>0.0325; 0.0771</td>
<td>0.0403; 0.0996</td>
</tr>
</tbody>
</table>
An X-ray powder diffraction study showed that 6 was different from both 7 and 8.

References


