Coordination Chemistry of the Ditopic Ligand 4-[6-(2-Pyridyl)-2-pyridyl]-6-(2-pyridyl)pyrimidine: Encapsulation of Nitrate by [2×2]Grid Complexes

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We describe herein the synthesis, physical properties and crystal structures of metal complexes with the new ligand 6-(2-pyridyl)-4-[6-(2-pyridyl)-2-pyridyl]pyrimidine (**L**). Reactions of **L** with Ni^{II}, Co^{II}, Fe^{II}, Zn^{II} and Cu^{II} nitrates in a 1:1 ratio leads to the self-assembled tetranuclear [2×2] grid complexes **1**–**5** with encapsulated NO_3^- ions, as confirmed by the X-ray crystal structures of $[Ni_4\mathbf{L}_4(DMSO)_2(H_2O)_2](NO_3)(ClO_4)_7\cdot 4\,DMSO\cdot 6\,H_2O$ (**1**) and $[Co_4\mathbf{L}_4(DMF)_4](NO_3)(ClO_4)_7$ (**2**). The mononuclear copper(I) complex $[Cu\mathbf{L}(PPh_3)_2]ClO_4\cdot 2\,(CH_3CN)$ (**6**) and the binuclear $[Cu_2\mathbf{L}_2(CN)(PPh_3)_2]ClO_4$ (**7**) were synthesized from **L** and $[Cu(PPh_3)_3]Cl$.

Introduction

Self-assembly of specially designed metal complexes may afford a variety of unusual topologies, e.g. molecular grids, boxes, ladders and helicates.[1] These highly ordered structures may have well defined cavities which can act as binding pockets for substrates. Self-assembled metal complexes may therefore be useful as receptors, sensors or catalysts. The sizes and shapes of such cavities may be tuned by varying both the ligand structure and the metal ion in order to achieve optimal interaction between the cavity and a substrate.

The development of anion selective receptors is an important topic in chemistry. Reported examples of anion binders based on polynuclear complexes include a "molecular square" assembled from four Ni^{II} ions and tetrazine-derived ligands with a tetrafluoroborate guest,[2] molecular Pd^{II}/Pt^{II} triangles containing ClO_4^- or PF_6^-[3] and a grid-like $Fe^{II}_2Ru^{II}_2$ complex of a 4,6-bis(2,2′-bipyridyl)pyrimidine ligand which encloses chloride in its central cavity.[4] We have recently demonstrated the usefulness of polynuclear metal complexes as ionophores for the construction of anion-selective electrodes.[5]

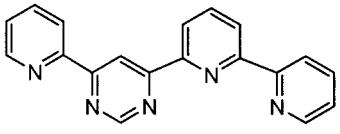
The selective recognition of nitrate is of particular interest since this ion has been implicated in groundwater contamination and is present in high concentrations in certain waste waters. The majority of reported receptors for nitrate are based on H-bonding interactions.[6] Funnel-shaped tri- and hexanuclear Pd^{II}/Pt^{II} complexes incorporating a nitrate at the bottom of the funnel by very weak coordinative bonds are a rare exception.[7] In a recent communication we reported the crystal structure of a tetranuclear nickel(II) complex forming a [2×2] grid structure and incorporating a nitrate in its cavity.[8]

Attempts to isolate the same complex with a Cl^- guest, as observed for the corresponding octahedral M^{II} complexes of the symmetric ligand 4,6-bis(2,2́-bipyridyl)pyrimidine,[4] failed. Interestingly, subtle structural modifications have a significant influence on the host-guest chemistry of the self-assembled complexes.

Herein we present a detailed investigation of the coordination chemistry and metal-induced self-assembly of **L** with the divalent 3d-metal ions Ni^{II}, Fe^{II}, Zn^{II}, Co^{II} and Cu^{II}. In addition, we have explored complex formation of **L** with Cu^{I} ions which prefers a tetrahedral over an octahedral metal coordination as observed in $\mathbf{L}_4M_4$ grid complexes.

Results and Discussion

Details of the synthesis and X-ray structure of the ditopic ligand **L** which has one tridentate and one bidentate metal binding site have been reported elsewhere.[9]



L

Complexes of **L** with Ni^{II}, Co^{II}, Fe^{II}, Cu^{II} and Zn^{II} were prepared by mixing the ligand and suitable metal salts in organic solvents or water. Crystalline compounds were filtered off, washed with isopropanol and dried under high vacuum. Sometimes recrystallisation from different solvents was necessary to obtain crystals suitable for X-ray analysis.

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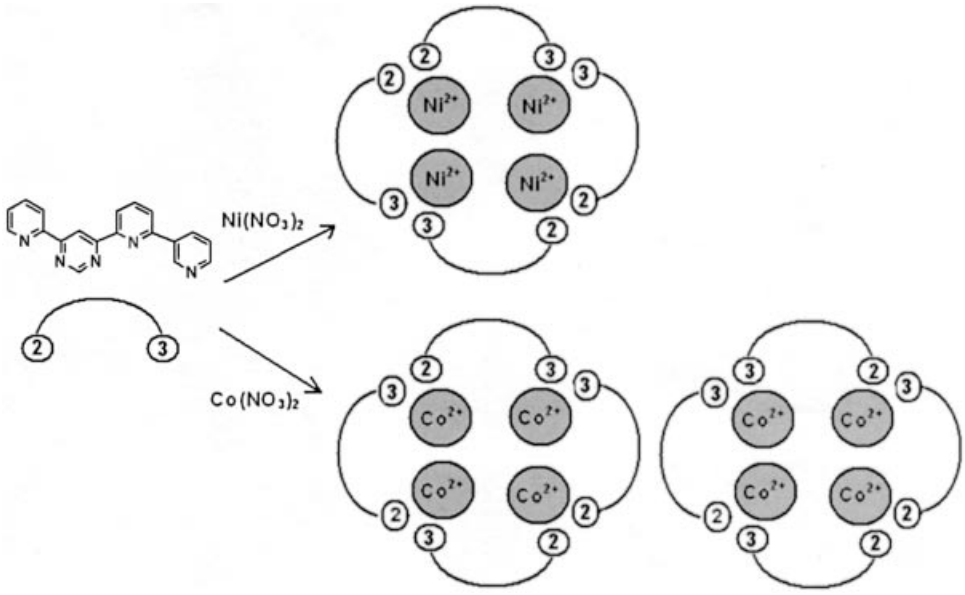

Scheme 1. Tetranuclear grid complexes **1** and **2** are pseudocoordination isomers.

Complex formation is accompanied by a colour change from colourless to yellow in the case of the Ni^{II} complex **1** to red-brown in the case of Co^{II} complex **2**, to dark-blue for the Fe^{II} complex **3** and to blue in the case of the Cu^{II} complex **5**. In the case of the Zn^{II} complex **4**, no significant colour changes were observed. C, H, N analyses of the isolated compounds were in agreement with following formulae: $[Ni_4\mathbf{L}_4(DMSO)_2(H_2O)_2](NO_3)(ClO_4)_7\cdot 4\,DMSO\cdot 6\,H_2O$ (**1**), $[Co_4\mathbf{L}_4(DMF)_4](NO_3)(ClO_4)_7$ (**2**), $[Fe_4\mathbf{L}_4(H_2O)_4](NO_3)(ClO_4)_7\cdot 6\,H_2O$ (**3**), $[Zn_4\mathbf{L}_4(H_2O)_4](NO_3)_4Cl_4\cdot 2\,H_2O$ (**4**) and $[Cu_4\mathbf{L}_4(H_2O)_4](NO_3)_4(ClO_4)_4\cdot 2\,H_2O$ (**5**). For **1** and **2** the tetranuclear structures were confirmed by X-ray analyses. Since **L** is unsymmetrical, isomerism of the metal complexes is possible (Scheme 1).

The complex cation of **1** displays C_2 symmetry and contains two crystallographically independent nickel ions (Figure 1). The four nitrogen atoms of two different molecules of **L** and two oxygen atoms of the *cis*-orientated DMSO and H_2O molecules, respectively, constitute the distorted octahedral environment of Ni(1).[8] Ni(2) is coordinated by six nitrogen atoms of the tridentate sites of two molecules of **L**. Four nickel atoms are arranged at the corners of an almost ideal square [Ni(1)···Ni(2) = 6.170 Å, Ni(1)···Ni(2a) = 6.235 Å, Ni(1)–Ni(2)–Ni(1a) = 88.4°, Ni(2)–Ni(1)–Ni(2a) = 91.6°].

The tetranuclear complex cation of **2**[10] is shown in Figure 2. There is disorder of the ligand connecting Co(1) and Co(2) through its bidentate/tridentate and tridentate/bidentate sites [the site occupation factor for the disordered **L**/DMF ligands on Co(1)–Co(3) is 50:50] and probably for the ligand between Co(2) and Co(3) as well. The DMF ligands could not be localised at these positions. The coordination environments of the cobalt atoms can be described as N_5O or N_6 for Co(1), N_5O or N_6 for Co(2) and N_5O or N_6 for Co(3). The coordination environment of Co(4) is N_4O_2 which is formed from four nitrogen atoms from two

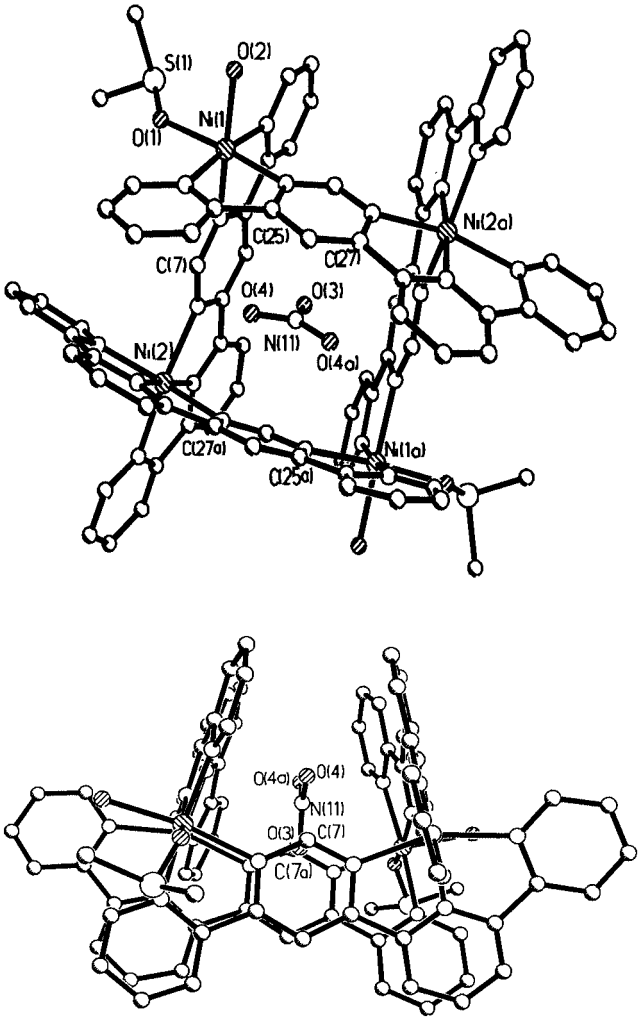

Figure 1. View of the structure of the complex cation of **1** with the enclosed nitrate ion. Hydrogen atoms are omitted for clarity.

different molecules of **L** and two oxygen atoms from DMF molecules.

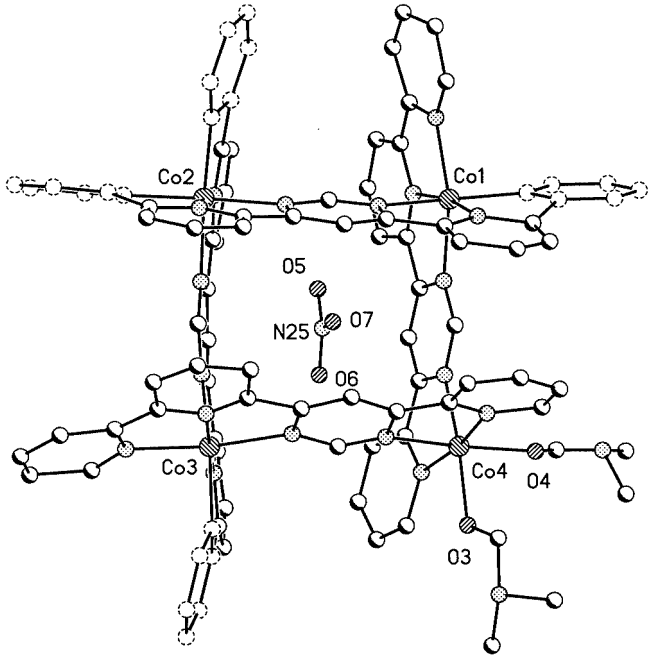

Figure 2. View of the structure of the complex cation of **2** with an enclosed nitrate ion.

The presence of two (depicted in Scheme 1) or more isomers in the crystal of **2** might be the origin of the disorder problems. The Co···Co distances average 6.25 Å which is slightly larger than Ni···Ni distances (6.20 Å) in **1** but significantly shorter than in a related tetracobalt (II) complex derived from a 4,6-bis(2,2′-bipyridyl)pyrimidine ligand (6.49 Å).[11] This illustrates that replacement of one of the two tridentate sites in the latter ligand by a bidentate site has a substantial effect on the cavity size of the self-assembled structure. The difference between the M···M distances in **1** and **2** corresponds to double the difference between the ionic radii of the corresponding metals. Consequently, both a variation in the ligand structure and metal ion size should enable fine tuning of the cavity size in complexes of this type. We have used a series of divalent transition-metals with different atomic radii for construction of [2×2] grids with different cavity sizes for guest binding. Crystallographic data for the Ni^{II} and Co^{II} grids allow us to estimate the M···M distances in the Fe^{II}, Zn^{II} and Cu^{II} [2×2] grids as 6.29, 6.14 and 6.08 Å, respectively, based on the published radii for the high-spin metal ions.[12]

A NO_3^- anion is trapped in the hydrophobic central cavity in both **1** and **2**, the latter being formed from the heterocyclic aromatic rings of the ligands. The molecular plane of the NO_3^- is coplanar to one ligand pair and perpendicular to the second (Figure 1). The close fit of the nitrate in **1** is confirmed by several short van der Waals contacts between the nitrate oxygens with the host, i.e. O(4)···C(25) = 2.814 Å, O(4a)···C(27) = 2.812 Å, O(4)···C(7) = 2.714 Å and O(3)···C(7) = 3.101 Å.[12] It is clear (Figure 1) that the mobility of nitrate within the cage is highly restricted since the two pairs of **L** are not exactly coplanar (interplanar angles are 38.2° and 33.4°) but display a roof-shaped arrangement. Binding of even slightly larger anions should be disfavoured since anion host contacts would be unfavourably short.

In the absence of crystallographic data for compounds **3**, **4** and **5**, a comparison of their solid state infrared spectra indicates that their structures might be related to those of **1** and **2**. Compounds **1**, **2** and **3** show characteristic strong bands of both nitrate (1384, 1384 and 1386 cm^{-1}) and perchlorate (1104, 1102 and 1107 cm^{-1}).[13] In the IR spectrum of **1** two $\nu_{(S=O)}$ peaks appear at 938 and 945 cm^{-1} confirming the presence of coordinated and uncoordinated molecules of DMSO. The presence of DMF molecules in **2** is indicated by presence in the IR spectrum of a strong peak at 1677 cm^{-1} which can be attributed to an amide $\nu_{(C=O)}$ vibration. Strong peaks in the IR spectra of **4** and **5** which are not observed in the spectrum of the free ligand with maxima at 1385, 1378, and 1386, 1378 cm^{-1}, respectively, can be assigned to $\nu_{(N=O)}$ vibrations of the expected two types of nitrate ion. The IR spectrum of **5** also exhibits a strong peak due to the perchlorate ions at 1105 cm^{-1}. All complexes **1**–**5** exhibit, in their IR spectra, a strong peak around 1385 cm^{-1} which in **1** and **2** can be unambiguously attributed to encapsulated nitrate. IR data support the assignment of the related tetranuclear structures of the cations of **3**, **4** and **5** with encapsulated nitrate ions.

To detect magnetic interactions between the metal centres, **2** was subjected to susceptibility measurements in the temperature range 1.7–300 K. Figure 3 shows the temperature dependence of $\chi_m \cdot T$. At 300 K, $\chi_m \cdot T$ equals 9.6 $cm^3 mol^{-1} K$ which roughly corresponds to the expected values for four uncoupled Co^{II} ions (d^7, S =). As T is lowered, $\chi_m \cdot T$ slowly decreases down to 50 K. Below this temperature, $\chi_m \cdot T$ drops abruptly down to 0.5 $cm^3 mol^{-1} K$. This behaviour indicates overall antiferromagnetic interactions between Co^{II} ions. The Curie temperature was evaluated as 23 K. For **3** a ^{57}Fe Mössbauer spectrum recorded at room temperature exhibited a major singlet characteristic of a low spin Fe^{II} species.

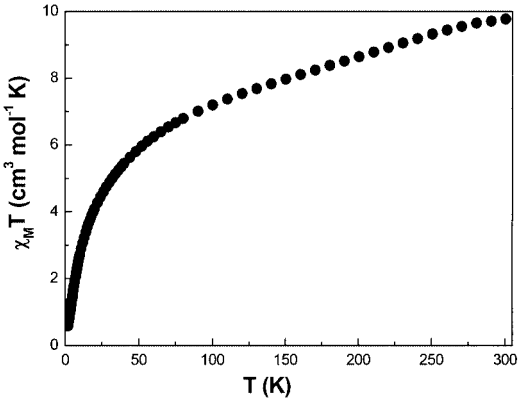

Figure 3. The temperature dependence of $\chi_m \cdot T$ for **2**.

Spectrophotometric titrations of **L** with Co^{II} and Fe^{II} in an acetone/water mixture revealed fast formation of $[\mathbf{L}_2M]^{2+}$ (increase of absorbance at 390 nm) but no further changes were observed immediately after addition of more then 0.5 equiv. of the metal ion (Figure 4). Formation of $\mathbf{L}_2M$ complexes could be confirmed by MALDI mass spectra of solutions containing **L** and M^{II} in a 1:1 ratio. When a MALDI mass spectrum of the Fe^{II} complex solution was recorded several hours after sample preparation, however, new signal corresponding to an $Fe_3\mathbf{L}_2$ fragment appeared.

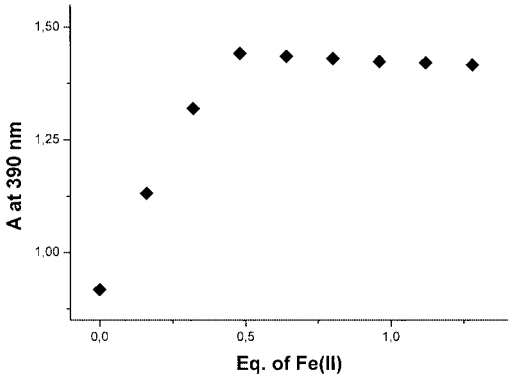

Figure 4. Increase of the 390 nm absorbance upon photometric titration of **L** (5×10^{-5} M) with Fe^{II}-tetrafluoroborate solution at 20 °C and pH 7.0 (spectra correspond to addition of Fe in steps of 0.16 equiv.).

These observations are consistent with fast formation of an $\mathbf{L}_2Fe$ species in which the terpyridine-like tridentate sites of **L** coordinate to the metal ion and slow conversion of this complex to the $\mathbf{L}_4Fe_4$ oligomer occurs. Any attempts to detect the intact $\mathbf{L}_4Fe_4$ complexes by mass spectrometric techniques (FAB, electrospray at variable concentrations, MALDI-TOF) failed, even for fresh solutions of crystalline samples of complexes **1** and **2**.

Complexes of L with Cu^I

While the tetranuclear [2×2] grid structure appears to be favoured with metal ions which can adopt octahedral coordination, **L** might form different types of self-assembled structures when metal ions with a preference for tetrahedral coordination are involved. We therefore explored the reaction of **L** with Cu^I ions which forms both tetrahedral complexes with 2,2′-bipyridyl type ligands and five coordinate complexes with *terpy* ligands, corresponding to the bidentate und tridentate sites of **L**, respectively.

The crystalline Cu^I complexes $[Cu\mathbf{L}(PPh_3)_2]ClO_4\cdot 2(CH_3CN)$ (**6**) and $[Cu_2\mathbf{L}_2(CN)(PPh_3)_2]ClO_4$ (**7**) could be obtained by treatment of **L** with $Cu^I(PPh_3)_3Cl$ followed by addition of $NaClO_4$ in acetone solution. Use of ClO_4^- promoted better crystallisation of the complexes.

The IR spectra of complexes **6** and **7** in the range 4000–400 cm^{-1} are quite similar and, as for **1**, **2**, **3**, **4** and **5**, show all the characteristic ligand peaks. The infrared spectra display bands for $\nu_{(C\equiv N)}$ at 2100 cm^{-1} (acetonitrile solvate) for **6** and 2080 cm^{-1} (bridging CN^-) for **7**, and bands for the perchlorate counterions at 1094 and 1098 cm^{-1} for **6** and **7**, respectively.[13] Crystals of **6** formed in acetonitrile appeared to lose solvent if left to stand in a solvent-free atmosphere.

ESI and MALDI mass spectra of solutions of **6** and **7** gave signals for mononuclear species. Major peaks in the spectra correspond to $[Cu\mathbf{L}]^+$ and $[Cu\mathbf{L}(OH)(OH_2)]^+$ with characteristic isotopic distributions for copper ions. Spectrophotometric titrations of ligand **L** with $[Cu(CH_3CN)_4]BF_4$ also indicate formation of a 1:1 **L**:Cu complex (Figure 5). Sharp isosbestic points were obtained in the range of 0 to 1 equiv. of Cu. The UV absorbance maxima of the complexes (about 330 nm) are shifted toward higher wavelengths relative to the free ligands (about 300 nm).

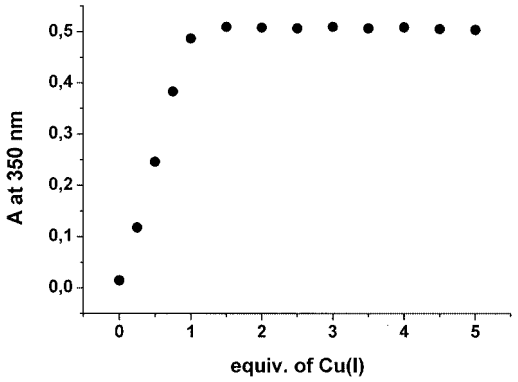

Figure 5. Increase of the 350 nm absorbance upon photometric titration of **L** (1×10^{-5} M) with $[Cu(CH_3CN)_4]BF_4$ solution at 20 °C (spectra correspond to addition of Cu in steps of 0.25 equiv.).

Crystal Structure of $[CuL(PPh_3)_2]ClO_4\cdot 2CH_3CN$ (6)

The solid-state structure of **6** was determined by X-ray crystallography (Table 1). The copper ion is four-coordinate (Figure 6) and bound to the two nitrogen atoms of **L** as well as two phosphorus atoms from PPh_3 groups. The geometry around the copper ion is distorted tetrahedral which is typical for Cu^I compounds, with angles ranging from 79.63(8) to 122.77(3)° (selected distances and angles are given in Table 1). The copper–phosphorus distances are nearly identical at 2.2461(8) and 2.2550(8) Å and are similar to the values in other Cu^I complexes.[14,15] The copper ion binds to the bidentate site of **L** with Cu–N distances of 2.052(2) and 2.083(2) Å. Very similar bonding parameters for the Cu^I ion were found in $[Cu(phen)(PPh_3)_2]^+$ and $[Cu(dmp)(PPh_3)_2]^+$ (where dmp is 2,9-dimethyl-1,10-phenanthroline).[16]

Table 1. Selected bond and lengths [Å] and angles [°] for **6**.

Cu(1)–N(1)	2.052(2)	N(1)–Cu(1)–P(1)	116.21(6)
Cu(1)–N(2)	2.083(2)	N(2)–Cu(1)–P(1)	107.82(6)
Cu(1)–P(1)	2.2461(8)	N(1)–Cu(1)–P(2)	109.08(6)
Cu(1)–P(2)	2.2550(8)	N(2)–Cu(1)–P(2)	113.24(6)
N(1)–Cu(1)–N(2)	79.63(8)	P(1)–Cu(1)–P(2)	122.77(3)

The heterocyclic fragments of **L** containing nitrogens N(3), N(4) and N(5) are coplanar whereas the heterocyclic fragment is tilted by 13.9°. The π-stacking (3.4 and 7.9 Å)

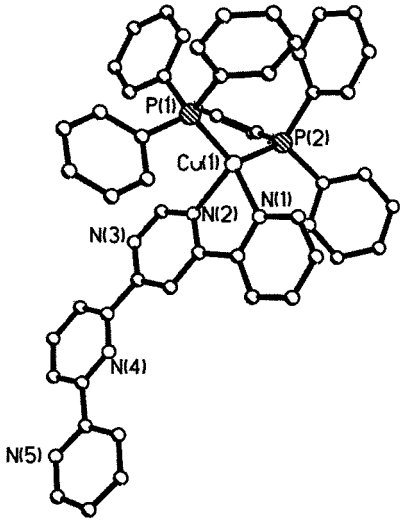

Figure 6. Molecular structure and numbering scheme for **6**. Hydrogen atoms are omitted for clarity.

of Cu**L** fragments can be observed in the crystal structure (Figure 7). The distances of the observed π-stacked units in **6** are approximately 3.4 and 7.9 Å.

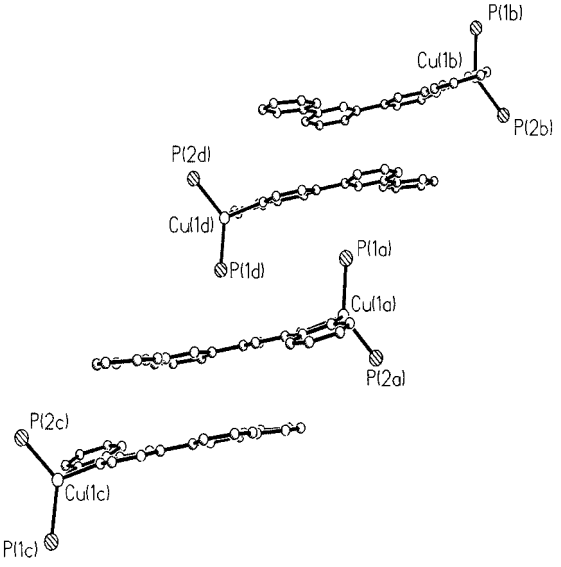

Figure 7. Stacking of complex cations in the crystal of **6**. Phenyl rings are omitted for clarity.

L contains both bi- and tridentate metal binding fragments. Interestingly, Cu^{I} prefers the bidentate bipyridyl-like binding site, although pentacoordinate Cu^{I} complexes with tridentate terpyridine and two monodentate coligands have been reported.[17] In each of the latter complexes, however, the metal ion coordination sphere is strongly distorted with one long metal–nitrogen contact and the complexes are not stable in solution and are spontaneously oxidised by air to the corresponding Cu^{II} complexes. In contrast, reported Cu^{I}-bipy-PPh_3 complexes are air stable in solution for days.[18] These facts indicate that bidentate bipyridyl is a better ligand for Cu^{I} than tridentate terpyridyl and explain the observed structures of **6** and **7** as well as the lack of oligomeric complex formation.

Sauvage and coworkers have designed a ligand system which consists of bidentate bipyridyl and tridentate terpyridyl fragments.[19] It was shown by electrochemical and spectroscopic methods that the preferred coordination mode for Cu^{I} is bidentate bipyridyl whereas for Cu^{II} it is tridentate terpyridyl. Similarly, the observation of a bidentate site preference for Cu^{I} should facilitate the design of mixed-metal self-assembled complexes of **L**.

Crystal Structure of $[Cu_2L_2(CN)(PPh_3)_2]ClO_4$ (7)

This structure (Table 2, Figure 8) reveals that the molecule of **7** contains two copper centres bridged by cyanide, traces of which were possibly present in the MeCN solvent. The bridging CN^- is disordered with respect to C/N coordination. Each copper ion exhibits a distorted tetrahedral geometry by binding to two nitrogen atoms from **L**, a phosphorus atom from PPh_3 and a nitrogen (carbon) atom from the CN group. The angles at the copper(I) atoms range from 78.84(9) to 127.87(7)°. In **7**, the copper–nitrogen distances are different, i.e. 2.089(2) and 2.090(2) Å to the heterocyclic nitrogen atoms and 1.930(2) Å to the nitrile nitrogen. The copper–phosphorus distance is 2.2094(8) Å. The copper–bpy nitrogen and copper–phosphorus distances are close to the corresponding values in **6**. The Cu–N(C)–C(N) angle is 164.5° and the Cu···Cu separation is 4.869 Å.

Table 2. Selected bond and lengths [Å] and angles [°] for **7**.

Cu(1)–N(1C)	1.930(2)	N(1C)–Cu(1)–N(3)	111.44(9)
Cu(1)–N(2)	2.089(2)	N(2)–Cu(1)–N(3)	78.84(9)
Cu(1)–N(3)	2.090(2)	N(1C)–Cu(1)–P(1)	127.87(7)
Cu(1)–P(1)	2.2094(8)	N(2)–Cu(1)–P(1)	105.10(6)
N(1C)–Cu(1)–N(2)	108.11(9)	N(3)–Cu(1)–P(1)	113.58(6)

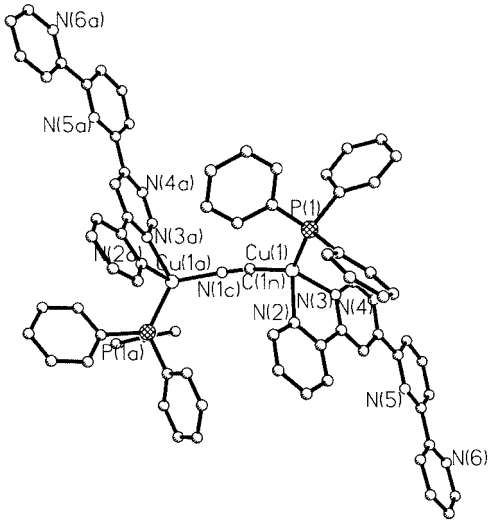

Figure 8. Molecular structure and numbering scheme for **7**. Hydrogen atoms are omitted for clarity.

Conclusions

We have reported here a novel polynucleating ligand which forms [2×2] grids with divalent 3d metals having different electronic structures, i.e. Ni^{II}, Co^{II}, Fe^{II}, Zn^{II} and Cu^{II}. As shown by magnetic measurements and Mössbauer spectroscopy, no significant interactions between metal centres occur in these compounds. We have also shown that the grids are formed only in the presence of NO_3^- ions and with divalent metal ions. Monovalent metal ions (e.g. Cu^I) both in the presence and absence NO_3^- form mono and dinuclear complexes. In both cases Cu^I prefers the bidentate to the tridentate binding site of the ligand.

Experimental Section

Materials and Procedures: Reagents and solvents were obtained from Aldrich, Acros or Fluka and used as received. 6-(2-Pyridyl)-4-[6-(2-pyridyl)-2-pyridyl]pyrimidine (**L**) was synthesized as previously reported.[9] The iron(II) and copper(I) complexes were synthesized and purified using typical high vacuum and/or Schlenk techniques.

Physical Measurements: ^{1}H NMR spectra were recorded on Bruker AC-300 (300.13 MHz) and Bruker AC-400 (400.13 MHz) spectrometers and chemical shifts are reported in ppm. Tetramethylsilane was used as an internal standard. Absorbance UV/Vis spectra of solutions were recorded on a Specord S100 spectrophotometer (Carl Zeiss Jena). IR spectra were obtained on a Perkin–Elmer 983 G spectrometer (as KBr pellets). Matrix-assisted laser desorption ionisation time of flight (MALDI-TOF) and LDI-TOF mass spectra were recorded on a Bruker Biflex III MS spectrometer in negative and positive linear modes. Variable-temperature magnetic susceptibility data (1.7–300 K) were acquired on powdered samples using a Quantum Design MPMS-5 SQUID magnetometer. Corrections for the diamagnetism of the ligand and Co^{II} cations were applied using Pascal's[20] constants; the diamagnetic contribution from the sample holder was also taken into account. The ^{57}Fe Mössbauer measurements were carried out using a conventional constant-acceleration spectrometer and the spectra were fitted using the MOSSFUN program.[21] Elemental analyses were performed by the Microanalytisches Laboratorium des Organisch-Chemischen Instituts der Universität Heidelberg.

Crystallographic Studies: Intensity data were collected at 173 K with a Bruker AXS SMART 100 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω scans, SADABS 10). Absorption corrections were applied. The structures were solved by direct methods using SHELXS-86[22,23] and refined by least-squares methods based on F^2 with all measured reflections using SHELX-97.[24] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and refined (Table 3).

CCDC-246323 (for **6**) and CCDC-246324 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Caution! Transition-metal perchlorate complexes are potentially explosive and should be handled with due care and in small quantities!

Synthesis of 1: See ref.[8]

Synthesis of 2: To a stirred solution of **L** (77 mg, 0.246 mmol) in acetone (5 mL) was added a solution of $Co(NO_3)_2{\cdot}4H_2O$ (63 mg, 0.249 mmol) in water (5 mL). A dark-red precipitate formed within 12 h which was filtered, washed with acetone and dried. The complex crystallised from DMF upon layering with a solution of $NaClO_4$ in acetone. Yield: 119 mg, (79%). $C_{88}H_{80}Cl_7Co_4N_{25}O_{35}$ (2451.63) calcd. C 41.75, H 3.19, N 13.83; found C 41.39, H 3.88, N 13.91. MS (MALDI) *m*/*z* (%): 370.2 (100) $[^{59}Co\mathbf{L} + e]^+$, 387.2 (90) $[^{59}Co\mathbf{L}(OH)]^+$. IR (KBr): $\tilde{\nu}$ = 1384 (N=O), 1102 (Cl=O), 1677 (C=O) cm^{-1}.

Synthesis of 3: To a stirred solution of **L** (20 mg, 0.064 mmol) in acetone (5 mL) was added a solution of $Fe(NO_3)_2{\cdot}6H_2O$ (17 mg, 0.064 mmol) in water (5 mL). A solution of $NaClO_4$ in acetone was then added to the resultant dark blue solution over 24 h. Complex **3** started to crystallise from this solution after 24 h and was filtered, washed with diethyl ether and dried in a high vacuum. Yield 34.8 mg (90%). $C_{76}H_{72}Cl_7Fe_4N_{21}O_{41}$ (2407.05): calcd. C 37.92, H 3.01, N 12.22; found C 38.51, H 3.21, N 12.31. MS (MALDI) *m*/*z* (%): 678.5 (100) $[^{56}Fe\mathbf{L}_2 + e]^+$, 791.4 (70) $[^{56}Fe_3\mathbf{L}_2]^+$. IR (KBr): $\tilde{\nu}$ = 1386 (N=O), 1107 (Cl=O) cm^{-1}.

Synthesis of 4: To a stirred solution of **L** (65 mg, 0.21 mmol) in acetone (5 mL) was added a solution of $Zn(NO_3)_2{\cdot}4H_2O$ (58 mg, 0.21 mmol) in water and a solution of $ZnCl_2$ (31mg, 21 mmol) in water (5 mL). The white precipitate which formed was filtered off, washed with diethyl ether and dried in high vacuum. Yield 82.2 mg (79%). $Zn_4C_{76}H_{64}Cl_4N_{24}O_{18}$ (2004.8): calcd. C 45.53, H 3.22, N

Table 3. Crystal data and structure refinements for **6** and **7**.

	6	**7**
Formula	$[Cu\mathbf{L}(Ph_3P)_2](ClO_4){\cdot}2CH_3CN$	$[Cu_2\mathbf{L}_2(Ph_3P)_2(CN)](ClO_4)$
Empirical formula	$C_{59}H_{49}ClCuN_7O_4P_2$	$C_{75}H_{56}ClCu_2N_{11}O_4P_2$
M	1080.98	1399.78
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pbcn*
a [Å]	14.2661(12)	21.7976(13)
b [Å]	28.741(2)	18.7664(12)
c [Å]	13.7571(12)	15.8443(10)
V [Å] ^{3}	5347.0(8)	6481.3(7)
Z	4	4
Scan range θ [°]	1.42 to 26.38	1.43 to 26.37
μ [mm^{-1}]	0.573	0.809
Unique reflections	10937	6633
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0449, wR_2 = 0.1046	R_1 = 0.0402, wR_2 = 0.0883

16.77; found C 46.51, H 3.20, N 16.34. MS (MALDI) *m/z* (%): 375.74 (100) [^{64}Zn**L** + e]$^+$, 377.0 (60) [^{66}Zn**L** + e]$^+$, 379.74 (50) [^{68}Zn**L** + e]$^+$, 393.74 (54) [^{64}Zn**L**(H_2O) + e]$^+$, 395.0 (32) [^{66}Zn**L**(H_2O) + e]$^+$, 397.74 (26) [^{68}Zn**L**(H_2O) + e]$^+$. IR (KBr): $\tilde{\nu}$ = 1385 and 1378 (N=O) cm^{-1}.

Synthesis of 5: To a stirred solution of **L** (73 mg, 0.23 mmol) in acetone (5 mL) was added a solution of $Cu(NO_3)_2{\cdot}4H_2O$ (44 mg, 0.22 mmol). The blue precipitate was filtered off, washed with diethyl ether and dried. The complex crystallised from DMF upon layering with a solution of $NaClO_4$ in acetone. Yield 89.3 mg (68%). $C_{76}H_{64}Cl_4Cu_4N_{24}O_{34}$ (2253.46): calcd. C 40.51, H 2.06, N 14.92; found C 41.34, H 2.10, N 13.74. MS (MALDI) *m/z* (%): 374.0 (100) [^{63}Cu(**L**)]$^+$, 376.0 (60) [^{65}Cu(**L**)]$^+$, 392.0 (54) [^{63}Cu(**L**)(H_2O)]$^+$, 394.0 (32) [^{65}Cu(**L**)(H_2O)]$^+$. IR (KBr): $\tilde{\nu}$ = 1386 and 1378 (N=O), 1105 (Cl=O) cm^{-1}.

Synthesis of 6 and 7: To a stirred solution of **L** (45 mg, 0.14 mmol) in dry acetonitrile (3 mL) was added a solution of $Cu(PPh_3)_3Cl$ (90 mg, 0.15 mmol) in dry acetonitrile (5 mL). The clear orange solution was stirred for 30 min at 40 °C. After 15 min a small amount of a white precipitate started to form. This was filtered off and to the filtrate was added $NaClO_4$ in acetone (1 mL). Complex **6** was filtered off from this solution after 48 h. Complex **7** crystallised from the second solution after 24 h. For **6**: Yield 26 mg (17%). $C_{59}H_{49}ClCuN_7O_4P_2$ (1080.98): calcd. C 65.55, H 4.57, N 9.07; found C 64.75, H 3.98, N 8.51. MS (MALDI) *m/z* (%): 374.0 (100) [^{63}Cu**L** + e]$^+$, 376.0 (60) [^{65}Cu**L** + e]$^+$, 636.1 (10) [^{63}Cu**L**Ph_3P + e]$^+$, 638.1 (5) [^{65}Cu(**L**)(Ph_3P) + e]$^+$. IR (KBr): $\tilde{\nu}$ = 2100 (CN), 1094 (Cl=O) cm^{-1}. For **7**: Yield 39 mg (19%). $C_{69}N_{11}H_{56}P_2ClO_4Cu_2$ (1399.78): calcd. C 64.35, H 4.03, N 11.01; found C 62.97, H 3.88, N 10.79. MS (MALDI) *m/z* (%): 374.0 (100) [^{63}Cu(**L**)]$^+$, 376.0 (60) [^{65}Cu(**L**)]$^+$, 636.1 (10) [^{63}Cu**L**Ph_3P + e]$^+$, 638.1 (5) [^{65}Cu**L**(Ph_3P) + e]$^+$, 400.1 (10) [^{63}Cu**L**(CN) + e]$^+$, 402.1 (5) [^{65}Cu**L**(CN) + e]$^+$. IR (KBr): $\tilde{\nu}$ = 2080 (CN), 1098 (Cl=O) cm^{-1}.

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[1] G. F. Swigers, T. J. Malefetse, C. Name, *Chem. Rev.* **2000**, *100*, 3483.
[2] C. S. Campos-Fernandez, R. Clerac, K. R. Dunbar, *Angew. Chem. Int. Ed.* **1999**, *38*, 3477.
[3] a) R.-D. Schnebeck, E. Freisinger, B. Lippert, *Chem. Commun*. **1999**, 675; b) R.-D. Schnebeck, E. Freisinger, B. Lippert, *J. Am. Chem. Soc.* **2000**, *122*, 1381.
[4] D. M. Bassani, J.-M. Lehn, K. Fromm, D. Fenske, *Angew. Chem. Int. Ed.* **1998**, *37*, 2364.
[5] B. Ahlers, K. Cammann, S. Warzeska, R. Krämer, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2141.
[6] a) L. H. Uppadine, M. G. B. Drew, P. D. Beer, *Chem. Commun.* **2001**, 291; b) K. Kavallieratos, R. A. Sachleben, G. J. Van Berkel, B. A. Moyer, *Chem. Commun.* **2000**, 187; c) K. Niikura, A. P. Bisson, E. V. Anslyn, *J. Chem. Soc., Perkin Trans. 2* **1999**, 1111; d) S. Mason, T. Clifford, L. Seib, K. Kuczera, K. Bowman-James, *J. Am. Chem. Soc.* **1998**, *120*, 8899; e) R. C. Jagessar, D. H. Burns, *Chem. Commun.* **1997**, 1685; f) J. Wiorkiewicz-Kuczera, K. Kuczera, C. Bazzicalupi, A. Bencini, B. Valtancoli, A. Bianchi, K. Bowman-James, *New J. Chem.* **1999**, *23*, 1007 and references cited therein; g) P. D. Beer, M. G. B. Drew, R. Jagessar, *J. Chem. Soc., Dalton Trans.* **1997**, 881; h) P. D. Beer, M. G. B. Drew, D. Hesek, R. Jagessar, *J. Chem. Soc., Chem. Commun.* **1995**, 1187; i) R. J. Motekaitis, A. E. Martell, J.-M. Lehn, E. I. Watanabe, *Inorg. Chem.* **1982**, *21*, 4253; j) Q. Qian, G. S. Wilson, K. Bowman-James, H. H. Girault, *Anal. Chem.* **2001**, *73*, 497 and references cited therein; k) Metalated calixarene receptor: M. Staffilani, K. S. B. Hancock, J. W. Steed, K. T. Holman, J. L. Atwood, R. K. Juneja, R. S. Burkhalter, *J. Am. Chem. Soc.* **1997**, *119*, 6324.
[7] R.-D. Schnebeck, E. Freisinger, B. Lippert, *Angew. Chem. Int. Ed.* **1999**, *38*, 168.
[8] R. Krämer, L. Kovbasyuk, H. Pritzkow, *New J. Chem.* **2002**, *26*, 516.
[9] L. Kovbasyuk, M. Hoppe, H. Pritzkow, R. Krämer, *Eur. J. Inorg. Chem.* **2001**, *5*, 1353.
[10] The quality of the crystals available did not allow a satisfactory structure determination but the connectivity could be determined. We have therefore refrained from publishing details of the structure. $P\bar{1}$, a = 16.0805(10), b = 6.7139(10), c = 25.3261(15) Å, α = 82.427(2), β = 78.958(2), γ = 67.935(1)°, V = 6178.10 Å^3, Z = 2, $\theta_{max.}$ = 20.82°, μ = 0.64 mm^{-1}, R_1 = 0.1599, wR_2 = 0.2341 [for $I > 2\sigma(I)$]. Two CH_3 groups belonging to DMF molecules are not localised because of high disorder.
[11] a) E. Breuning, U. Ziener, J.-M. Lehn, E. Wegelius, K. Rissanen, *Eur. J. Inorg. Chem.* **2001**, 1515; b) G. S. Hanan, D. Volkmer, U. S. Schubert, J.-M. Lehn, G. Baum, D. Fenske, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, N17, 1842 and references cited therein.
[12] S. S. Batsanov, *J. Chem. Soc., Dalton Trans.* **1998**, *10*, 1541.
[13] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York, **1986**.
[14] L. M. Engelhardt, C. Pakawatchai, A. H. White, P. C. Healy, *J. Chem. Soc., Dalton Trans.* **1985**, 125.
[15] K. T. Brooks, D. C. Finnen, J. R. Kirchhoff, A. A. Pinkerton, *Acta Crystallogr. Sect. C* **1994**, *50*, 1696.
[16] J. R. Kirchhoff, D. R. McMillin, W. R. Robinson, D. R. Powell, A. T. McKenzie, S. Chen, *Inorg. Chem.* **1985**, *24*, 3928.
[17] E. W. Ainscough, A. M. Brodie, S. L. Ingham, J. M. Waters, *J. Chem. Soc., Dalton Trans.* **1994**, 215.
[18] S. W. Keller, S. Lopez, *J. Am. Chem. Soc.* **1999**, *121*, 6306.
[19] A. Livoreili, C. O. Dietrich-Buchecker, J.-P. Sauvage, *J. Am. Chem. Soc.* **1994**, *116*, 9399.
[20] I. M. Kolthoff, P. J. Elving, *Treat. Anal. Chem.* **1963**, *4*, Part 1.
[21] D. Adler, H. Spiering, P. Gütlich, *Inorg. Chem.* **1987**, *26*, 3840.
[22] G. M. Sheldrick, SADABS, Bruker AXS, Madison, WI, USA, **1999**.
[23] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**.
[24] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

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