A Versatile Approach to the Intramolecular Organization of Two Bipyridine-Like Chelating Units in a Polytopic Ligand

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Dedicated to Prof. Dr. Dieter Sellmann on the occasion of his 60th birthday

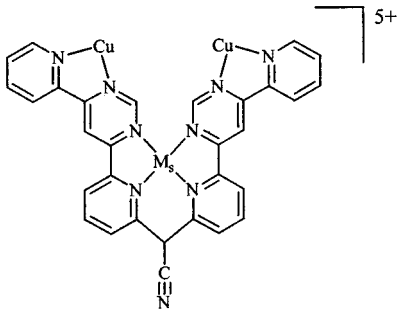
Keywords: Bioinorganic chemistry / Copper / Enzyme mimics / Ligand design / Catalysis

The synthesis of four novel polypyridyl ligands, in which two 4,6-[bis(2-pyridyl)]pyrimidine units are covalently linked by spacer groups –S– (**1**), –S–S– (**2**), –Se– (**7**), and –Se–Se– (**6**), is reported. A new unsymmetrical dinucleating ligand **4** was isolated as a by-product in the synthesis of **2** and has been characterized by X-ray crystallography. Copper(II) complexes $[(\mathbf{1})Cu](NO_3)_2{\cdot}5H_2O$ and $[(\mathbf{7})Cu](ClO_4)_2{\cdot}6H_2O$ have been isolated, spectroscopic data for which are consistent with tetradentate N_4 coordination by the ligands. In situ prepared polynuclear copper(II) complexes of **1** and **7** show different catalytic activities in the cleavage of the phosphodiester 2-hydroxypropyl *p*-nitrophenyl phosphate. This might be a consequence of the influence of the covalent spacer (S or Se) on the preorganization of two bipyridine-like chelating units in $[LCu]^{2+}$, which bind two catalytic Cu^{2+} ions.

Introduction

In many enzymes, chemical transformations are mediated by the cooperation of two active site metal ions. This functional motif is particularly prominent in phosphoryl transfer enzymes including phosphodiesterases, nucleases, phosphatases, and DNA/RNA-polymerases.[1] During the last 15 years, many dinuclear model complexes have been designed to improve the understanding of metal−metal cooperation in such enzymes.[2] Preorganization, i.e. intermetal distance and relative orientation of coordination polyhedra, is a parameter that is of fundamental importance with regard to reactivity. In practice, it is difficult to design a model system that allows systematic variation of the preorganization while other factors that influence the reactivity are kept constant. Breslow has described dinuclear zinc(II) complexes in which two (chelator) Zn subunits are covalently linked by spacer groups of varying size. This approach requires laborious synthesis of a set of appropriate ligands and allows only rough tuning of metal−metal separation.[3] We have recently described trinuclear complexes $(L)M_sCu_2$, in which a "structural" metal ion M_s is coordinated to the tetradentate site and two "functional" Cu^{2+} ions bind to the bipyridine-like chelating groups of the ligand[4] (Scheme 1). The catalytic activity of this complex in the cleavage of a phosphodiester was shown to be strongly dependent on the nature of the structural metal ion M_s.

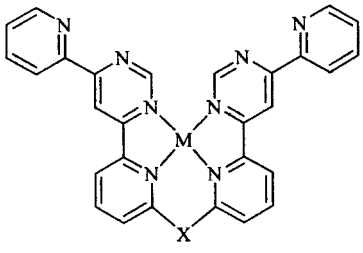
This was interpreted in terms of different catalyst conformations, i.e. fine-tuning of the preorganization of the two functional Cu^{2+} ions, depending on the ionic radius of M_s and on its tendency to distort the N_4-M_s coordination plane.



Scheme 1. Trinuclear complex $(\mathbf{L})M_sCu_2$

$(L)M_sCu_2$ constituted the first example of an abiotic allosteric catalyst; M_s is a noncovalent modifier of the reactivity, but is not directly involved in the reaction. In this context, we report herein on the synthesis of related polypyridyl ligands and their metal complexes.

Variation of the spacer group that covalently links the dipyridylpyrimidine subunits (Scheme 2) is tested as an additional possible means of controlling organization of the bipyridine-like chelating groups and of tuning the reactivity of the polynuclear complexes.



Scheme 2

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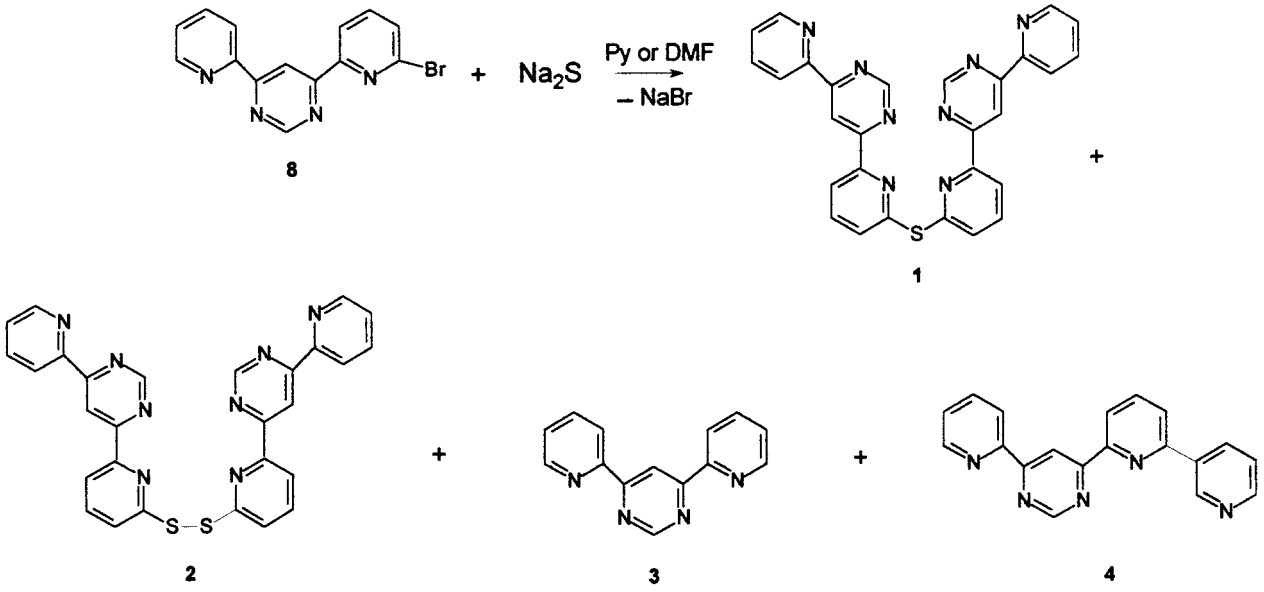
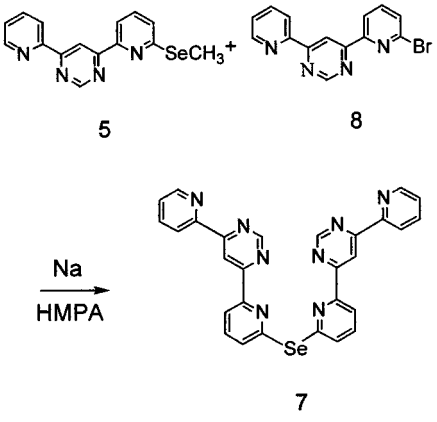


Scheme 3. Synthesis of **1**, **2**, and **4**

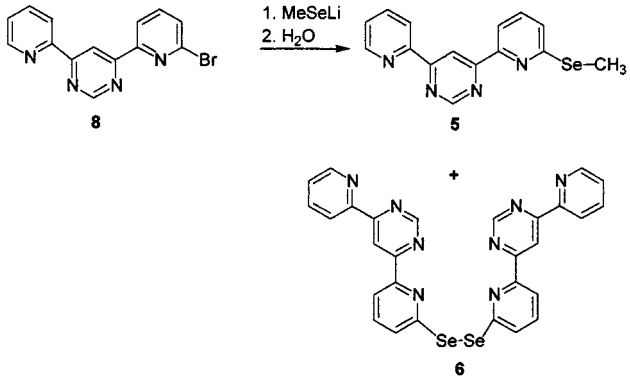
Results and Discussion

Preparation of the novel polypyridyl ligands **1**, **2**, **6**, and **7** is outlined in Scheme 3, Scheme 4, and Scheme 5. The synthesis of the precursor 4-(6-bromo-2-pyridyl)-6-(2-pyridyl)pyrimidine (**8**) is described elsewhere.[5]



Scheme 4. Synthesis of **7**

The synthesis of compounds with a py−S−py moiety by reaction of pyridyl bromides and thiols has been described previously. In particular, bis(2-pyridyl) sulfide has been isolated following reaction of 2-mercaptopyridine with 2-bromopyridine and K_2CO_3 in DMF.[6] In the present case, the thiol was not isolated but is involved as an intermediate in the formation of **1** from the bromo compound and Na_2S. Oxidation of the thiol intermediate by oxygen during workup gives the disulfide compound **2**. The yields of compounds **1** and **2** were found to be dependent on the ratio of **8** to Na_2S. For optimal yields of **1** and **2**, the requisite **8**/Na_2S ratios proved to be 1:1.5 and 1:5, respectively.



Scheme 5. Synthesis of **5** and **6**

As a side product, 4-[6-(2-pyridyl)-2-pyridyl]-6-(2-pyridyl)pyrimidine (**4**) was isolated when the reaction described in Scheme 3 was conducted in pyridine. The mechanism of its formation is unclear. Ligand **7** was obtained in analogy to a reported method for the synthesis of bis(2-pyridyl) selenide[12] from halopyridines and $LiSeCH_3$. In the first step, methyl 6-[6-(2-pyridyl)-4-pyrimidinyl]-2-pyridyl selenide (**5**) was synthesized by reaction of CH_3Li, selenium, and **8**.

Cleavage of the Se−CH_3 bond was achieved in the second step by treatment with metallic sodium, resulting in the formation of a selenolate intermediate, which displaced the bromine in **8** to give **7** (Scheme 4). **6** was unexpectedly obtained as a side product in the synthesis of **5** (Scheme 5), and its yields could be optimized using a higher ratio of CH_3Li/Se to **8**. Presumably, a selenol(ate) intermediate is involved and the Se−Se bond is formed by air oxidation. Ligands **1** and **2** were obtained as pale-yellow powders, **6** and **7** as yellow powders, and were characterized by mass spectrometry, NMR spectroscopy, and C,H,N analysis. The crystal structure of **4** (white needles) was elucidated by X-ray analysis.

Compound **4** was formed as a by-product when the reaction outlined in Scheme 4 was performed in pyridine, but not when DMF was used as solvent. Thus, the reaction is rationalized in terms of a C−C coupling of **8** with the pyridine solvent. The mechanism of this process is not clear, but activation of pyridine for a C−C coupling reaction at its C-2 position under relatively mild conditions (90−100 °C, 7 h, Na_2S) is, to the best of our knowledge, quite unusual. Thus, for unambiguous determination of the structure of **4**, it was subjected to X-ray crystallographic analysis. Suitable crystals of **4** were obtained by isothermal crystallization from acetone. The molecular structure of **4**, showing the numbering scheme used, is presented in Figure 1. Selected bond lengths and angles are given in Table 1.

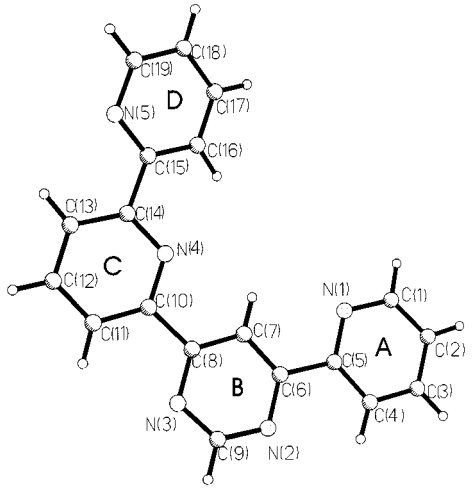


Figure 1. Molecular structure of **4** showing numbering scheme

The unit cell is monoclinic and contains four molecules of **4**. The rings A, B, and C are coplanar, whereas the plane of ring D forms an angle of 30° with the A, B, and C planes. The bond lengths and angles in **4** are typical for pyridine and pyrimidine heterocycles.[7]

Mononuclear copper(II) complexes of **1** and **7** were prepared by mixing the ligands and suitable metal salts in organic solvents and were isolated as green powders. Attempts to crystallize these complexes failed. C,H,N analyses of the solids were consistent with hydrated 1:1 complexes with the formulae [Cu(**1**)]$(NO_3)_2\cdot 5H_2O$ and [Cu(**7**)]$(ClO_4)_2\cdot 6H_2O$. Copper(II) complexes of **2** and **6** could not be isolated, although mass spectrometry indicated the formation of 1:1 complexes. Evidence of the decomposition of the complexes by redox processes was noted. Thus, solutions show the gradual appearance of new bands at around 450 nm in their UV/Vis spectra, similar to $[(bpy)_2Cu^{I}]^+$.

Table 1. Selected bond lengths and angles in **4**

N(1)−C(1)	1.34(2)	C(4)−C(5)	1.38(2)
N(1)−C(5)	1.34(2)	C(6)−C(7)	1.38(2)
N(2)−C(9)	1.33(2)	C(7)−C(8)	1.39(2)
N(2)−C(6)	1.34(2)	C(8)−C(10)	1.49(2)
N(3)−C(9)	1.33(2)	C(10)−C(11)	1.39(2)
N(3)−C(8)	1.34(2)	C(11)−C(12)	1.38(2)
N(4)−C(14)	1.34(2)	C(12)−C(13)	1.37(2)
N(4)−C(10)	1.34(2)	C(13)−C(14)	1.39(2)
N(5)−C(19)	1.34(2)	C(14)−C(15)	1.49(2)
N(5)−C(15)	1.35(2)	C(15)−C(16)	1.39(2)
C(1)−C(2)	1.38(2)	C(16)−C(17)	1.38(2)
C(2)−C(3)	1.37(2)	C(17)−C(18)	1.38(2)
C(3)−C(4)	1.38(2)	C(18)−C(19)	1.38(2)
C(5)−C(6)	1.49(2)		
C(1)−N(1)−C(5)	116.76(13)	C(7)−C(6)−C(5)	121.89(12)
C(9)−N(2)−C(6)	115.44(13)	C(6)−C(7)−C(8)	118.12(13)
C(9)−N(3)−C(8)	115.64(13)	N(3)−C(8)−C(7)	121.14(13)
C(14)−N(4)−C(10)	118.06(12)	N(3)−C(8)−C(10)	117.08(13)
C(19)−N(5)−C(15)	117.06(13)	C(7)−C(8)−C(10)	121.78(13)
N(1)−C(1)−C(2)	124.09(15)	N(3)−C(9)−N(2)	128.18(15)
C(3)−C(2)−C(1)	118.31(15)	N(4)−C(10)−C(11)	122.58(13)
C(2)−C(3)−C(4)	119.09(15)	N(4)−C(10)−C(8)	116.09(12)
C(3)−C(4)−C(5)	118.82(14)	C(11)−C(10)−C(8)	121.32(13)
N(1)−C(5)−C(4)	122.92(13)	C(12)−C(11)−C(10)	118.49(15)
N(1)−C(5)−C(6)	116.07(12)	C(13)−C(12)−C(11)	119.42(15)
C(4)−C(5)−C(6)	121.01(12)	C(12)−C(13)−C(14)	118.95(15)
N(2)−C(6)−C(7)	121.46(13)	N(4)−C(14)−C(13)	122.40(14)
N(2)−C(6)−C(5)	116.65(12)	N(4)−C(14)−C(15)	116.49(13)
C(13)−C(14)−C(15)	121.09(13)	C(17)−C(16)−C(15)	119.16(15)
N(5)−C(15)−C(16)	122.30(13)	C(16)−C(17)−C(18)	119.10(15)
N(5)−C(15)−C(14)	116.34(13)	C(19)−C(18)−C(17)	118.12(15)
C(16)−C(15)−C(14)	121.35(13)	N(5)−C(19)−C(18)	124.26(15)

The MALDI-TOF mass spectra of solutions of the complexes feature major peaks corresponding to $[Cu(\mathbf{1})]^+$, $[Zn(\mathbf{6})]^+$, and $[Cu(\mathbf{7})]^+$ patterns with characteristic isotopic distributions for the relevant metal ions. Attempts to isolate zinc(II) complexes of the prepared ligands were successful only in the case of **6**, for which [Zn(**6**)]$(CH_3COO)_2$ was obtained.

The NMR data of the mononuclear zinc complex of **6** are consistent with tetradentate metal coordination. The ^1H NMR spectrum (solution in $CDCl_3$) is consistent with C_2 symmetry of the complex. In the NOESY spectrum, the signal due to the Pym-5 proton shows an intense cross-peak with the signal due to the Py′-3/Py-3 protons. This indicates that the pyrimidine ring is *cis*-oriented with respect to the internal pyridine ring, as expected for tetradentate coordination of the ligand.

Information about the copper coordination sphere in solution was obtained from EPR spectroscopic data. The EPR spectra of [Cu(**1**)]$(NO_3)_2\cdot 5H_2O$ and [Cu(**7**)]$(NO_3)_2\cdot 6H_2O$ in DMSO glass were recorded at liquid nitrogen temperature. In the spectrum of [Cu(**1**)]$(NO_3)_2\cdot 5H_2O$, specifically the part of perpendicular orientation, *N*-superhyperfine coupling with the nitrogen donor atoms is observed, but is poorly resolved. The spin Hamiltonian parameters obtained are $g_\perp = 2.06$, $g_\parallel = 2.26$, $A_\parallel = 166$ G, and $g_\perp = 2.07$, $g_\parallel = 2.32$, $A_\parallel = 151$ G for

[Cu(**1**)](NO$_3$)$_2$·5H$_2$O and [Cu(**7**)](NO$_3$)$_2$·6H$_2$O, respectively. These parameters are consistent with the presence in both complexes of a tetrahedrally distorted square-planar copper environment with a $d_{x^2-y^2}$ ground state ($g_{\|} > g_{\perp}$).[8] The values of the spin Hamiltonian parameters of these complexes agree well with those reported for flattened N_4 tetrahedral complexes of Cu^{2+} [8,9] and are distinctly different from those of square-planar tetradentate Cu^{2+} in the previously described LCu (L = ligand shown in Scheme 1), $g_{\|}$ = 2.207, $A_{\|}$ = 196 G.[10]

The EPR parameters indicate the degree of distortion of the CuN_4 moiety from planarity, which determines the preorganization of the bidentate, bipyridine-like chelating units in the mononuclear complexes. A near-planar N_4 coordination in LCu (L = ligand shown in Scheme 1), as suggested by the $g_{\|}$ and $A_{\|}$ values, was confirmed by a crystal structure determination of [LCu(MeOH)]ClO_4.[10] In this complex, two pyrimidine 2-H protons approach their van der Waals contact distance. Any decrease in the C−X−C bond angle at spacer atom X (Scheme 2), or any increase in the X−C bond length, should give rise to an increased helical twist of the mononuclear complex with tetrahedral distortion of the CuN_4 plane in order to minimize steric repulsion between the pyrimidine 2-H protons. Thus, the apparent increase in the degree of tetrahedral distortion in the order X = C, S, Se becomes understandable in terms of specific bonding parameters of these spacing atoms.

In our previous study on complexes of ligand L (Scheme 1), spectrophotometric titrations gave evidence concerning the metal complex species present in solution. Attempts to characterize the solution chemistry of the Cu complexes of **1** and **7** under the same conditions (water/DMSO, 3:1) were complicated by insufficient solubility of the ligands in the absence of the metal ion and by slow complex formation.

Fast complexation was observed in a 1:1 dichloromethane/acetonitrile medium, and UV titrations were indicative of the formation of both mononuclear and trinuclear complexes. Sharp isosbestic points were obtained for 0−1 equiv. of Cu when 5% DMSO was added to the solvent mixture (Figure 2 and Figure 3).

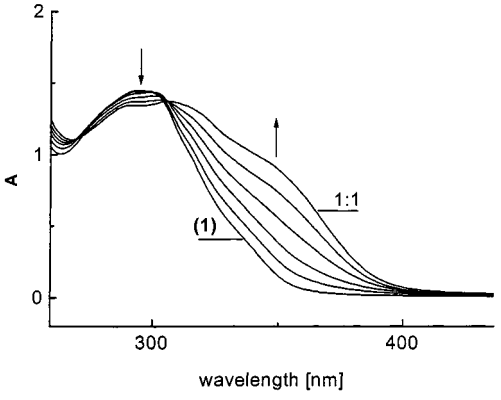


Figure 2. Spectrophotometric titration of **1** with copper(II) perchlorate in a CH_3CN/CH_2Cl_2 (1:1) solution containing 5% DMSO at 20 °C from 0−1 equiv. (spectra correspond to addition of Cu in 0.2-equiv. steps)

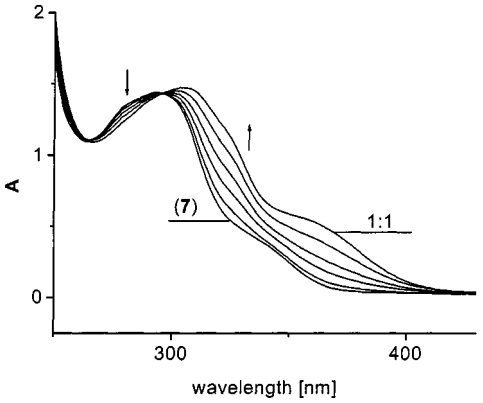


Figure 3. Spectrophotometric titration of **7** with copper(II) perchlorate in a CH_3CN/CH_2Cl_2 (1:1) solution containing 5% DMSO at 20 °C from 0−1 equiv. (spectra correspond to addition of Cu in 0.2-equiv. steps)

The absorbance maxima of the complexes (about 310 nm) are shifted toward higher wavelengths relative to the free ligands (about 290 nm). Interestingly, the competitive solvent DMSO inhibits the formation of polynuclear complexes; no significant spectral changes are observed on addition of > 1 equiv. of Cu (see also the absorbance diagrams, Figure 4 and Figure 5).

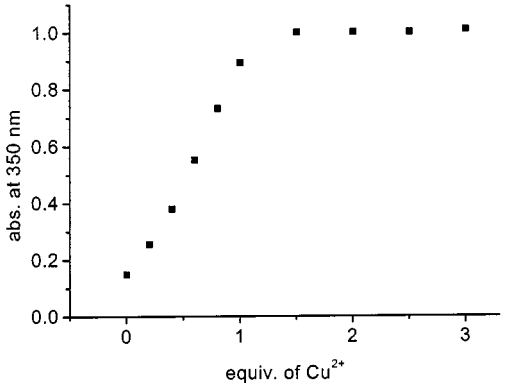


Figure 4. Increase of 350 nm absorbance on photometric titration of **1** ($5\cdot10^{-5}$ M) with copper(II) perchlorate solution; for conditions, refer to Figure 2

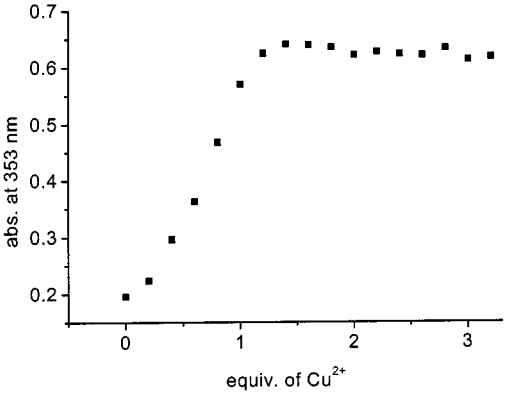


Figure 5. Increase of 353 nm absorbance on photometric titration of **7** ($5\cdot10^{-5}$ M) with copper(II) perchlorate solution; for conditions, refer to Figure 3

In a dichloromethane/acetonitrile (1:1) solution in the absence of DMSO, the lack of an isosbestic point for the titration 0 → 1 equiv. of Cu suggests the formation of an intermediate species when the ligand is present in excess {possibly formed by coordination of free ligand pyridyl groups to axial sites in [Cu(**1**,**7**)]; such species may not be stable in competitive solvents such as DMSO}. In clear contrast to the titrations shown in Figure 2 and Figure 3, the spectrum changes significantly when > 1 equiv. of Cu^{2+} is added and a rather sharp end point is seen after the addition of 3 equiv. of Cu (no further changes beyond 3 equiv. of Cu). For simplicity, Figure 6 shows selected spectra of free ligand **1** and at 1:1, 2:1, 3:1, and 4:1 Cu/**1** ratios.

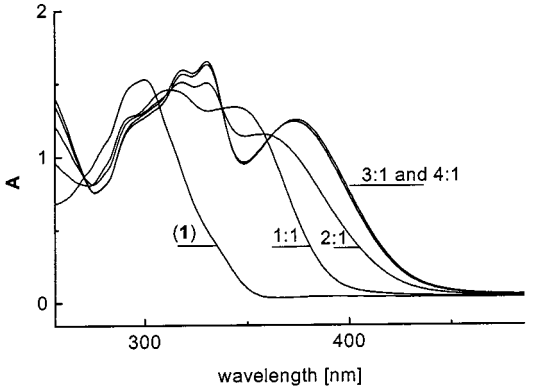


Figure 6. Spectrophotometric titration of **1** with copper(II) perchlorate in CH_3CN/CH_2Cl_2 (1:1) at 20 °C from 0−4 equiv. (spectra correspond to addition of Cu in 1-equiv. steps)

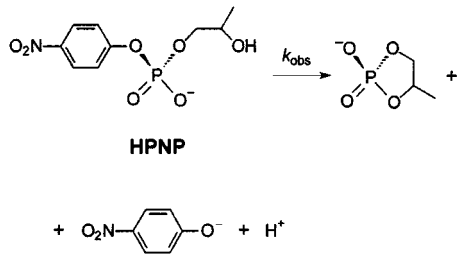
Very similar behaviour is observed for the Cu complexes of **7**, with the trinuclear complex showing nearly identical absorbance maxima.

Since catalytic studies (see below) are performed in buffered water/DMSO (3:1) mixtures, we tried to explore the formation of [(**1**)Cu] complexes under these conditions. The spectrum of [(**1**)Cu]$(ClO_4)_2$ is very similar to that observed in CH_2Cl_2/MeCN (1:1). On addition of Cu^{2+}, only subtle spectral changes are observed, polynuclear complexes apparently being much less stable than in the CH_2Cl_2/MeCN medium.

Interestingly, the spectral changes are qualitatively the same as those seen in CH_2Cl_2/CH_3CN (Figure 6), i.e. an increase in the absorbance maximum at 320 nm (Figure 6: 320 and 340 nm), an isosbestic point at 340 nm (Figure 6: 340 nm), a decrease in the absorbance at 350 nm, an isosbestic point at 370 nm (Figure 6: 360 nm, not sharp), and an increase in the absorbance at 390 nm (Figure 6: maximum at 375 nm).

By comparison with the spectra in Figure 6, we estimated that a maximum of 5% of the polynuclear complex was present after addition of 5 equiv. of Cu^{2+} under the conditions of Figure 7 (HPNP was replaced by the less reactive dimethyl phosphate).

We have examined the reactivity of in situ prepared polynuclear copper(II) complexes of **1** and **7** toward the phosphodiester 2-hydroxypropyl *p*-nitrophenyl phosphate (HPNP), an RNA analogue which is widely used to examine phosphoesterase activity of metal complexes. Intramolecular cyclization of this phosphodiester is easily followed photometrically by monitoring the 400 nm absorbance of the released nitrophenolate (Scheme 6).



Scheme 6. Intramolecular cleavage of the phosphodiester 2-hydroxypropyl *p*-nitrophenyl phosphate (HPNP)

Kinetic studies were performed at varying Cu^{2+} concentrations in a buffered water/DMSO (3:1) mixture at pH = 7.0, with 10^{-4} M ligand **1** or **7** and $5\cdot10^{-4}$ M HPNP (these conditions were used to allow direct comparison with previously reported kinetic studies on the complexes shown in Scheme 1).

As expected, the 1:1 complexes were found to be practically ineffective in HPNP cleavage. However, the rate increases dramatically when polynuclear complexes are formed upon addition of Cu^{2+}. The profiles in Figure 7 are consistent with our spectrophotometric observations. The concentration of the reactive polynuclear species would seem to increase linearly with Cu^{2+} concentration. This indicates that the bidentate sites of [(**1**)Cu]$^{2+}$ are far from being saturated with metal ions and that the polynuclear complex must be present in low concentration.

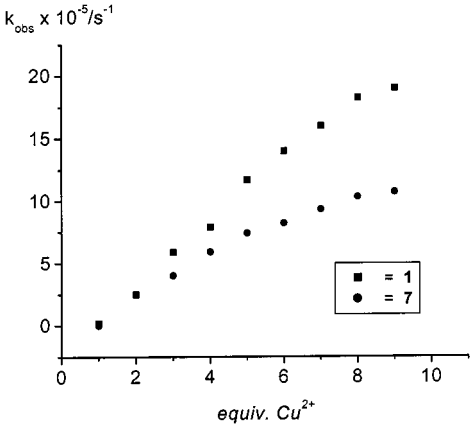


Figure 7. k_{obs} for cleavage of HPNP ($5\cdot10^{-4}$ M) in solutions containing **1** (10^{-4} M) and **7** (10^{-4} M) and varying copper(II) nitrate concentrations; water/DMSO (3:1), pH = 7.0, buffer 5 mM 3-morpholinopropanesulfonic acid (MOPS), T = 20 °C; cleavage by free Cu^{2+} is negligible

This is consistent with our results obtained by photometric titration of [(**1**)Cu]$^{2+}$ with Cu^{2+} in water/DMSO (3:1). In analogy with our previous work on LCu complexes (L = ligand shown in Scheme 1), we suggest that the reactive spe-

cies is a trinuclear complex. Under the conditions of Figure 7, a trinuclear Cu complex of L (Scheme 1) forms quantitatively with a slight excess of Cu and cleaves HPNP with $k_{obs} = 27 \cdot 10^{-5}$ s^{-1}.[4] Given that complexes $[(\mathbf{1})Cu_3]^{6+}$ and $[(\mathbf{7})Cu_3]^{6+}$ are the reactive species and are present only in low concentration, they must be even more reactive than $[LCu_3]^{5+}$ (L = ligand shown in Scheme 1). It is unlikely that a dinuclear complex $[(\mathbf{1}, \mathbf{7})Cu_2]^{4+}$ is the reactive species since the in situ prepared dinuclear Cu^{2+} complex of 4,6-di(2-pyridyl)pyrimidine (which compares to the aforementioned dinuclear complex with bridging pyrimidine) cleaves HPNP only with $k_{obs} = 8 \cdot 10^{-6}$ s^{-1} under the conditions of Figure 7.

The higher tendency of complex LCu (Scheme 1) to bind additional Cu^{2+} ions might, in part, be a result of the negative charge of the ligand, which, to some extent, compensates the electrostatic repulsion between the metal ions in the polynuclear complexes. It is evident from Figure 7 that the reactive Cu^{2+} species of **1** and **7**, presumably the trinuclear complexes, show different reactivity towards HPNP. In the presence of nine equivalents of Cu^{2+}, the complex of **1** is more efficient by a factor of 1.7. Thus, the spacer group (S or Se) clearly influences the catalytic activity of the complexes. In principle, variation of both the spacer groups X and the metal ion M (Scheme 2) promises to offer a versatile approach for fine-tuning the preorganization of two bipyridine-like chelating units and of their coordinated metal ions. Unfortunately, in preliminary attempts to prepare heteronuclear Ni^{II}/Cu^{II} and Pd^{II}/Cu^{II} complexes, it became evident that Ni and Pd are displaced from the tetradentate site by Cu. This is in contrast to the previously reported complexes of L (L = ligand shown in Scheme 1), which are not susceptible to metal exchange.[4]

Experimental Section

General Remarks: Reagents were obtained from either Aldrich or Fluka and were used as received. 4-(6-Bromo-2-pyridyl)-6-(2-pyridyl)pyrimidine was synthesized as described previously.[5] The barium(II) salt of 2-hydroxypropyl *p*-nitrophenyl phosphate was prepared by a reported method.[11] All reactions were carried out in dry solvents (HPLC grade) under nitrogen using Schlenk techniques. Workup was performed using technical grade solvents without protection from air. − Preparative column chromatography was carried out on Merck silica gel 60 (0.040−0.063 mm). Retention factors (R_f) were determined using Macherey−Nagel alumina TLC plates. − ^{1}H,^{13}C COSY and NOESY NMR spectra were recorded with Bruker AC-300 (300.13 MHz) and Bruker AC-400 (400.13 MHz) spectrometers; chemical shifts are reported in ppm. Tetramethylsilane was used as an internal standard. − IR spectra were obtained with a Perkin−Elmer 983 G spectrometer (samples in KBr pellets). − FD and EI mass spectra were recorded with a Finnigan MAT 8230 instrument. MALDI-TOF mass spectra were recorded with a Bruker Biflex TOF-MS spectrometer in negative or positive linear mode. − Elemental analyses were performed by the Microanalytisches Laboratorium des Organisch-Chemischen Instituts der Universität Heidelberg and by the Microanalytisches Laboratorium des Instituts für Anorganische und Analytische Chemie der Universität Mainz.

Ligand Syntheses

Bis{6-[6-(2-pyridyl)-4-pyrimidinyl]-2-pyridyl} Sulfide (1): This ligand was prepared as outlined in Scheme 3. A solution of $Na_2S \cdot 10H_2O$ (2.1 g, 8.1 mmol) in DMF (10 mL) was added to a stirred solution of 4-(6-bromo-2-pyridyl)-6-(2-pyridyl)pyrimidine (1.7 g, 5.4 mmol) in DMF (20 mL). The reaction mixture was stirred for 7 h at 90−100 °C, then allowed to cool, and kept at room temperature for 12 h. The white-yellow precipitate was collected by filtration, washed with DMF (15 mL), and dried in vacuo for 24 h (0.01 mbar). Water (100 mL) was added to the residue, and the product was extracted with chloroform (3 × 100 mL). The combined chloroform extracts were dried with $MgSO_4$, filtered, and concentrated to dryness, and the residue was dried in vacuo for 6 h. Yield: 0.8 g (30%), $R_f = 0.56$ (acetone/hexane, 3:7). − $C_{28}H_{18}N_8S$ (498.56): calcd. C 67.46, H 3.64, N 22.48, S 6.43; found C 67.21, H 3.61, N 22.32, S 5.99. − IR (KBr): $\tilde{\nu}$ [ν(S−R)] = 1100 cm^{-1} s. − ^{1}H NMR ($CDCl_3$): δ = 7.41 (ddd, 1 H, $J_{5,4}$ = 7.6 Hz, $J_{5,6}$ = 4.8 Hz, $J_{5,3}$ = 1.4 Hz, Py-5), 7.74 (dd, 1 H, $J_{5,4}$ = 7.8 Hz, $J_{5,3}$ = 0.9 Hz, Py′-5), 7.85 (td, $J_{4,5}$ = 7.8 Hz, $J_{4,3}$ = 7.8 Hz, Py-4), 7.91 (t, $J_{4,5}$ = 7.8 Hz, $J_{4,3}$ = 7.8 Hz, 1 H, Py′-4), 8.42 (dt, $J_{3,4}$ = 7.8 Hz, $J_{3,5}$ = 1.0 Hz, 1 H, Py-3), 8.46 (dd, $J_{3,4}$ = 7.8 Hz, $J_{3,5}$ = 1.0 Hz, 1 H, Py′-3), 8.75 (dq, $J_{6,5}$ = 4.8 Hz, $J_{6,4}$ = 0.9 Hz, 1 H, Py-6), 9.21 (d, $J_{2,5}$ = 1.4 Hz, 1 H, Pym-5), 9.314 (d, $J_{2,5}$ = 1.3 Hz, 1 H, Pym-2). − MS (FD); *m*/*z* (%): 498.2 (100) [M$^+$].

1,2-Bis{6-[6-(2-pyridyl)-4-pyrimidinyl]-2-pyridyl} Disulfide (2): A solution of $Na_2S \cdot 10H_2O$ (1.6 g, 6.5 mmol) in DMF (10 mL) was added to a stirred solution of 4-(6-bromo-2-pyridyl)-6-(2-pyridyl)pyrimidine (0.39 g, 1.3 mmol) in DMF (30 mL). The reaction mixture was stirred for 12 h at 90−100 °C, then allowed to cool, and kept at room temperature for 12 h. The solvent was evaporated at 50 °C in a rotary evaporator. Water (100 mL) was then added and the by-products **1**, **3**, and **4** were extracted from the resulting suspension with chloroform (3 × 200 mL). The aqueous phase was treated with acetic acid (10 mL) and the solution was stirred for 1 h. The product **2** was then extracted with chloroform (3 × 200 mL). The combined chloroform extracts were dried with $MgSO_4$, filtered, and concentrated to dryness. Yield: 70 mg (10%). − $C_{28}H_{18}N_8S_2$ (530.62): calcd. C 63.38, H 3.42, N 21.12, S 12.08; found C 64.11, H 3.01, N 20.82, S 11.89. − IR (KBr): $\tilde{\nu}$ [ν(R−S)] = 1093 cm^{-1} s. − ^{1}H NMR ([D$_6$]DMSO): δ = 7.02 (t, $J_{4,5}$ = 7.8 Hz, Py-5), 7.98 (dd, $J_{4,5}$ = 7.8 Hz, $J_{3,5}$ = 0.9 Hz, 1 H, Py-4), 8.00 (td, $J_{4,5}$ = 7.8 Hz, $J_{3,5}$ = 7.8 Hz, 1 H, Py′-4), 8.08 (t, $J_{4,5}$ = 7.8 Hz, 1 H, Py′-3), 8.35 (d, $J_{4,5}$ = 1.3 Hz, 1 H, Py′-5), 8.45 (dd, $J_{4,3}$ = 7.8 Hz, $J_{3,5}$ = 1.0 Hz, 1 H, Py-3), 8.70 (dq, $J_{6,5}$ = 4.7 Hz, $J_{4,6}$ = 0.8 Hz, 1 H, Py-6), 9.15 (s, 1 H, Pym-5), 9.35 (s, 1 H, Pym-2). − MS (FD); *m*/*z* (%): 530.4 (100) [M$^+$].

4-[6-(2-Pyridyl)-2-pyridyl]-6-(2-pyridyl)pyrimidine (4): A solution of $Na_2S \cdot 10H_2O$ (0.57 g, 2.3 mmol) in pyridine (10 mL) was added to a stirred solution of 4-(6-bromo-2-pyridyl)-6-(2-pyridyl)pyrimidine (0.7 g, 2.3 mmol) in pyridine (20 mL). The reaction mixture was stirred for 12 h at 90−100 °C, then allowed to cool, and kept at room temperature for 12 h. The solvent was evaporated at 50 °C in a rotary evaporator. Water (100 mL) was then added and **1**, **3**, and **4** were extracted from the resulting suspension with chloroform (3 × 200 mL). The combined chloroform extracts were dried with $MgSO_4$, filtered, and concentrated to dryness. The mixture of products **1**, **3**, and **4** was separated by column chromatography using 10% acetone in hexane as eluent. − 1st fraction: **3**, yield 0.18 g (42%), $R_f = 0.75$ (acetone/hexane, 3:7). − $C_{14}H_{10}N_4$ (234.26): calcd. C 71.78, H 4.30, N 23.92; found C 71.83, H 4.31, N 23.70. − ^{1}H NMR ([D$_6$]DMSO): δ = 7.43 (ddd, 2 H, $J_{3,5}$ = 1.1 Hz, $J_{4,5}$ = 7.8 Hz, $J_{5,6}$ = 4.8 Hz, Py-5), 7.89 (td, 2 H, $J_{3,4}$ = 7.8 Hz, $J_{4,6}$ =

1.2 Hz, Py-4), 8.52 (dt, 2 H, Py-3), 8.80 (ddd, 2 H, Py-6), 9.36 (d, 2 H, $J_{2,5}$ = 1.1 Hz, Pym-5), 9.39 (d, 2 H, Pym-2). − MS (FD); *m/z* (%): 234.3 (100) [M^+]. The data are identical to those reported in the literature.[10] − 2nd fraction: **4**, yield 0.2 g (35%), R_f = 0.68 (acetone/hexane, 3:7). − ^{1}H NMR ([D$_6$]acetone): δ = 7.37 (dd, *J* = 8.3 Hz, *J* = 5.0 Hz, 1 H), 7.45 (dd, *J* = 8.3 Hz, *J* = 5.0 Hz, 1 H), 7.97 (m, 2 H), 8.03 (t, *J* = 8.3 Hz, 1 H), 8.564 (m, 3 H), 8.72 (d, *J* = 1.3 Hz, 1 H), 8.75 (d, *J* = 1.4 Hz, 1 H), 8.84 (d, *J* = 1.3 Hz, 1 H), 9.38 (s, 1 H, Pym-5), 9.51 (s, 1 H, Pym-2). − MS (FD); *m/z* (%): 311.4 (100) [M^+]. − 3rd fraction: **1**, R_f = 0.56 (acetone/hexane, 3:7).

Methyl 6-[6-(2-Pyridyl)-4-pyrimidinyl]-2-pyridyl Selenide (5): A solution of CH_3Li (1.6 M in Et_2O, 2.5 mL, 4 mmol) was added dropwise to a suspension of selenium (316 mg, 4 mmol) in absolute THF (25 mL) and stirring was continued for a further 30 min. The clear solution thus obtained was added dropwise to a solution of 4-(6-bromo-2-pyridyl)-6-(2-pyridyl)pyrimidine (1.25 g, 4 mmol) in absolute DMF (25 mL) and the resulting mixture was stirred for 15 min. The THF was then evaporated under high vacuum (0.01 mbar, 40 °C, 10 min) and the remaining DMF solution was stirred for 2.5 h at 70 °C and then cooled to room temperature. Water (200 mL) was added and the mixture was stirred for a further 12 h. The yellow precipitate formed was collected by filtration, recrystallized from chloroform, and purified by column chromatography eluting with MeOH/CH_2Cl_2 (1:100). Yield: 0.53 g (37%), R_f = 0.58 (hexane/acetone, 6:4). − $C_{15}H_{12}N_4Se$·MeOH (359.29): calcd. C 53.49, H 4.49, N 15.59; found C 52.16, H 4.38, N 14.73. − ^{1}H NMR ($CDCl_3$) δ = 2.64 (3 H, $SeCH_3$, *J* = 11.5 Hz), 7.43 (ddd, 1 H, $J_{4,5}$ = 7.8 Hz, $J_{5,6}$ = 4.8 Hz, $J_{3,5}$ = 0.9 Hz, Py-5), 7.43 [dd, 1 H, $J_{4,5}$ = 7.8 Hz, $J_{3,5}$ = 0.9 Hz, Py′-5 (?)],7.63 (t, 1 H, $J_{3,4}$ = 7.8 Hz, Py′-4), 7.89 (td, 1 H, $J_{3,4}$ = 7.8 Hz, $J_{4,6}$ = 1.9 Hz, Py-4), 8.25 [dd, 1 H, $J_{3,4}$ = 7.8 Hz, $J_{3,5}$ = 0.9 Hz, Py′-3 (?)], 8.50 (dt, 1 H, $J_{3,4}$ = 7.8 Hz, $J_{3,5}$ = 0.9 Hz, Py-3), 8.80 (dq, 1 H, $J_{5,6}$ = 4.6 Hz, $J_{4,6}$ = 0.9 Hz, Py-6), 9.33 (d, 1 H, $J_{2,5}$ = 1.3 Hz, Pym-2), 9.37 (d, 1 H, $J_{2,5}$ = 1.3 Hz, Pym-5). − MS (FAB+); *m/z* (%): 327.1 (40) [M^+ + H] with ^{78}Se, 329.1 (70) [M^+ + H] with ^{80}Se.

1,2-Bis{6-[6-(2-pyridyl)-4-pyrimidinyl]-2-pyridyl} Diselenide (6): The reaction was carried out in a similar fashion as described for **5**, but using a higher CH_3Li/Se to 4-(6-bromo-2-pyridyl)-6-(2-pyridyl)pyrimidine ratio. Thus, a solution of CH_3Li (1.6 M in Et_2O, 5 mL, 8 mmol) was added dropwise to a suspension of selenium (632 mg, 8 mmol) in absolute THF (25 mL) and stirring was continued for a further 30 min. The resulting solution was added dropwise to a solution of 4-(6-bromo-2-pyridyl)-6-(2-pyridyl)pyrimidine (1.25 g, 4 mmol) in absolute DMF (25 mL) and stirring was continued for 15 min. The THF was then evaporated under high vacuum (0.01 mbar, 40 °C, 10 min) and the remaining DMF solution was stirred for 2.5 h at 70 °C and then cooled to room temperature. Water (200 mL) was added and the mixture was stirred for a further 12 h. The yellow precipitate formed was collected by filtration, recrystallized from chloroform, and purified by column chromatography eluting with MeOH/CH_2Cl_2 (1:100). Yield: 0.69 g (27%), R_f = 0.46 (hexane/acetone, 6:4). − $C_{28}H_{18}N_8Se_2$·0.5 MeOH (640.44): calcd. C 53.45, H 3.15, N 17.50; found C 53.52, H 3.20, N 17.40. − ^{1}H NMR ($CDCl_3$): δ = 7.44 (ddd, 1 H, $J_{4,5}$ = 7.8 Hz, $J_{5,6}$ = 3.7 Hz, $J_{3,5}$ = 1.1 Hz, Py-5), 7.76 (t, 1 H, $J_{3,4}$ = 7.7 Hz, Py′-4), 7.90 (td, 1 H, $J_{3,4}$ = 7.7 Hz, $J_{4,6}$ = 1.8 Hz, Py-4), 8.02 [dd, 1 H, $J_{4,5}$ = 7.7 Hz, $J_{3,5}$ = 0.7 Hz, Py′-5 (?)], 8.32 [dd, 1 H, $J_{3,4}$ = 7.8 Hz, $J_{3,5}$ = 1.1 Hz, Py′-3 (?)], 8.50 (dt, 1 H, $J_{3,4}$ = 7.8 Hz, $J_{3,5}$ = 1.4 Hz, Py-3), 8.80 (dq, 1 H, $J_{5,6}$ = 3.7 Hz, $J_{4,6}$ = 0.8 Hz, Py-6), 9.34 (d, 1 H, $J_{2,5}$ = 1.3 Hz, Pym-2), 9.34 (d, 1 H, $J_{2,5}$ = 1.3 Hz, Pym-5). − MS (FAB+); *m/z* (%): 627.1 (40) [M^+ + H] with 2 × ^{80}Se, 625.1 (37) [M^+ + H] with ^{78}Se and ^{80}Se, 623.1 (22) [M^+ + H] with 2 × ^{78}Se. − MS (EI); *m/z*: 546.2 (100) [M^+ − Se] with ^{80}Se remaining, 544.2 (54) [M^+ − Se] with ^{78}Se remaining.

Bis{6-[6-(2-pyridyl)-4-pyrimidinyl]-2-pyridyl)} Selenide (7): According to a procedure for the preparation of bis(2-pyridyl) selenide,[12] a solution of methyl 6-[6-(2-pyridyl)-4-pyrimidinyl]-2-pyridyl selenide (**5**) (300 mg, 0.92 mmol) in hexamethylphosphortriamide (HMPA) (10 mL) was heated with small pieces of sodium (42 mg, 1.83 mmol) at 100 °C for 1.5 h. A solution of 4-(6-bromo-2-pyridyl)-6-(2-pyridyl)pyrimidine (288 mg, 0.92 mmol) in HMPA (10 mL) was then added dropwise. The red mixture was heated for 2.5 h at 120 °C. After cooling to room temperature, it was poured into cold water (100 mL) and the resulting suspension was stirred for 4 h. The brown precipitate formed was collected by filtration, washed with diethyl ether, and purified by column chromatography on SiO_2 eluting first with MeOH/CH_2Cl_2 (1:100) and then with pure $CHCl_3$. Yield 0.11 g (21%), R_f = 0.48 (hexane/acetone, 6:4). − $C_{28}H_{18}N_8Se$·MeOH (577.50): calcd. C 60.31, H 3.84, N 19.40; found C 61.13, H 3.98, N 18.13. − ^{1}H NMR ($CDCl_3$): δ = 7.47 (1 H, Py-5), 7.83 (2 H, Py-4, Py′-5), 7.92 (1 H, Py′-4), 8.44 (2 H, Py-3, Py′-3), 8.80 (1 H, Py-6), 9.25 (1 H, Pym-2), 9.33 (1 H, Pym-5). − MS (FAB$^+$); *m/z* (%): 547.2 (25) [M^+ + H] with ^{80}Se, 545.2 (15) [M^+ + H] with ^{78}Se.

Synthesis of the Complexes

[Cu(1)](NO$_3$)$_2$·5H$_2$O: To a stirred solution of **1** (12 mg, 0.024 mmol) in chloroform/methanol (1:3; 1 mL) was added a solution of $Cu(NO_3)_2$·3H_2O (6 mg, 0.024 mmol) in methanol (3 mL). The clear green solution thus obtained was stirred for 10 min at room temperature. After 1 h, diethyl ether (10 mL) was added, and the green precipitate formed was centrifuged off and dried under high vacuum for 6 h. Yield: 10 mg (54%). − $C_{28}H_{28}CuN_{10}O_{11}S$ (776.20): calcd. C 43.33, H 3.64, N 18.05; found C 42.75, H 3.38, N 18.11. − MS (MALDI); *m/z* (%): 561.5 (100) [^{63}Cu(**1**)]$^+$, 563.5 (54) [^{65}Cu(**1**)]$^+$, 596.5 (7) [^{63}Cu(**1**)(OH)]$^+$, 598.5 (6) [^{65}Cu(**1**)(OH)]$^+$.

[Cu(7)](ClO$_4$)$_2$·6H$_2$O: To a stirred solution of **7** (12 mg, 0.02 mmol) in chloroform (1 mL) was added a solution of $Cu(ClO_4)_2$·6H_2O (7.4 mg, 0.02 mmol) in acetonitrile (2 mL). The resulting mixture was stirred for 3 h at room temperature. The green precipitate formed was centrifuged off, washed with diethyl ether (10 mL), and dried under high vacuum for 4 h. Yield: 6.3 mg (38%). − $C_{28}H_{18}CuCl_2N_8O_8Se$·6$H_2O$ (915.91 g/mol): calcd. C 36.71, H 3.30, N 12.23; found C 35.68, H 2.99, N 10.92. − MS (MALDI); *m/z* (%): 607.2 (55) [^{63}Cu(**7**)]$^+$ with ^{78}Se, 609.2 (100) [^{63}Cu(**7**)]$^+$ with ^{80}Se, [^{65}Cu(**7**)]$^+$ with ^{78}Se, 611.2 (50) [^{65}Cu(**7**)]$^+$ with ^{80}Se.

[Zn(6)](CH$_3$COO)$_2$·CHCl$_3$·CH$_3$CN: A solution of 1,2-bis{6-[6-(2-pyridyl)-4-pyrimidinyl]-2-pyridyl} diselenide (**6**) (12 mg, 0.02 mmol) in chloroform (1.5 mL) was added dropwise to a stirred solution of $Zn(CH_3COO)_2$·2H_2O (4.4 mg, 0.02 mmol) in acetonitrile (2 mL).[13] After stirring for 3 h, a precipitate had formed, which was collected by filtration, washed with diethyl ether (2 × 5 mL), and dried in vacuo. Yield 8.4 mg (44%). − $C_{32}H_{24}N_8O_4Se_2Zn$·$CHCl_3$·CH_3CN (968.32): calcd. C 43.41, H 2.91, N 13.02; found C 42.08, H 3.00, N 12.73. − ^{1}H NMR ($CDCl_3$): δ = 1.90 (3 H, CH_3CN), 2.05 (6 H, CH_3COO), 7.53 (2 H, Py-5), 7.77 (2 H, Py′-4), 7.98 [4 H, Py-4 (?), Py′-5 (?)], 8.35 [4 H, Py-3 (?), Py′-3 (?)], 8.87 (2 H, Py-6), 9.21 (2 H, Pym-5), 9.43 (2 H, Pym-2). − MS (MALDI); *m/z* (%): 684.9 (66) [^{64}Zn(**6**)]$^+$ with 2 × ^{78}Se, 686.9 (91) [^{66}Zn(**6**)]$^+$ with 2 × ^{78}Se, [^{64}Zn(**6**)]$^+$ with 1 ×

^{78}Se and 1 × ^{80}Se, 688.9 (100) [^{66}Zn(**6**)]$^+$ with 1 × ^{78}Se and 1 × ^{80}Se, [^{64}Zn(**6**)]$^+$ with 2 × ^{80}Se, 690.9 (52) [^{66}Zn(**6**)]$^+$ with 2 × ^{80}Se.

Spectrophotometric Titrations: Stock solutions of **1** and **7** (10^{-3} M) were prepared in either DMSO (Figure 2, 3, 4, and 5) or CH_2Cl_2/CH_3CN (1:1) (Figure 6). These stock solutions were diluted with a CH_3CN/CH_2Cl_2 (1:1) mixture, and then the requisite amount of DMSO was added (5% v/v). The final ligand concentration in each case was $5\cdot10^{-5}$ M. Titrations were performed by addition of appropriate amounts of a $Cu(NO_3)_2\cdot3H_2O$ stock solution ($5\cdot10^{-4}$ M in CH_3CN). About 30 s after the addition of the copper salt, UV/Vis spectra were recorded at 25 °C. No further spectral changes with time were detectable on prolonged standing of the solutions.

Kinetics: Reaction solutions were prepared by combining appropriate amounts of the ligands **1** or **7** ($5\cdot10^{-4}$ M stock solutions in DMSO), $Cu(NO_3)_2\cdot3H_2O$ (2 mM stock solution in DMSO), the buffer 3-morpholinopropanesulfonic acid (MOPS) (0.5 M stock solution in H_2O, pH = 7.0), and water or DMSO solvent. Solutions were left to stand for 2 h. The reactions were initiated by addition of the substrate, 2-hydroxypropyl-*p*-nitrophenolphosphate (HPNP, 5 mM stock solution in H_2O). For the experiments summarized in Figure 7, the final concentrations in the reaction mixtures were 0.1 mM **1** or **7**, 0.5 mM HPNP, and 5 mM MOPS buffer in water/DMSO (3:1); the concentration of $Cu(NO_3)_2$ was varied from 0 to 1 mM. Transesterification of HPNP was followed spectrophotometrically by monitoring the release of *p*-nitrophenolate at 400 nm (ε = 18600 μ^{-1} cm^{-1}), considering the equilibrium *p*-nitrophenol/*p*-nitrophenolate at pH = 7.0 (pK_a = 7.15). The pseudo-first-order rate constants k_{obs} were determined from the initial rate of the reaction (< 5% conversion). All reported data are average values of at least three measurements (reproducibility within ± 15%). Measurements were made with a Carl-Zeiss-Technology Specord S 100 spectrophotometer at 20 °C.

Table 2. Crystal data and structure refinement for **4**

Empirical formula	$C_{19}H_{13}N_5$
Molecular mass	311.34
Crystal system	$P2_1/n$
Unit cell	
a [Å]	10.6(9)
b [Å]	7.6(7)
c [Å]	18.5(2)
β [°]	93.2(2)
Volume [Å^3]	1479.5(2)
Z	4
Calcd. density [g cm^{-3}]	1.398
Adsorp. coeff. [mm^{-1}]	0.088
F(000)	648
Crystal size [mm]	0.51 × 0.12 × 0.07
θ range [°]	2.17 ≤ θ ≤ 26.37
No. of reflections	9159
unique	3016
observed [$I > 2\sigma(I)$]	2077
Parameters	269
Final *R* indices	
*R*1 [$I > 2\sigma(I)$]	0.0391
*wR*2	0.1024
Largest diff.peak/hole [e/Å^3]	0.207/−0.180

X-ray Crystallographic Study of 4: Crystal data and details of the structure determination are listed in Table 2. Intensity data were collected at 173 K with a Bruker AXS CCD Smart 1000 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω scan). The structure was solved by direct methods and refined by least-squares methods based on F^2 with all measured reflections.[14] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in ideal positions and refined isotropically. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-149055. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.uk].

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