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Synthesis and Structures of Pyridinologous Linear Tri- and Tetrapyrrole Metal Complexes

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Summary. The Cu(II) complexes of a pyridinologous tri- and tetrapyrrole ligand which have recently been shown to be catalytically active were investigated by X-ray crystallography together with the Ni(II), Co(II), and Zn(II) complexes of the first ligand. These ligands displayed an astonishingly variable complexation behavior which uniquely allows to accommodate specific ligand field demands of a certain metal ion. This behavior seems to be an ideal prerequisite to provide catalytically active systems.

Keywords. Pyridinologous tripyrrole; Pyridinologous tetrapyrrole; Metal complexes; X-ray crystallography; Catalysis.

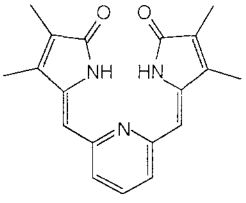
Zur Struktur von pyridinologen linearen Tri- und Tetrapyrrolmetallkomplexen

Zusammenfassung. Die Cu(II)-Komplexe eines pyridinologen Tri- und Tetrapyrrolliganden, für welche katalytische Aktivität nachgewiesen worden war, wurden zusammen mit den (Ni(II)-, Co(II)- und Zn(II)-Komplexen des erstgenannten Liganden röntgenstrukturanalytisch untersucht. Diese Liganden zeigten ein erstaunlich variables Komplexierungsverhalten, welches auf einzigartige Weise die Anpassung des Liganden an die spezifischen Bedürfnisse des Ligandfeldsystems eines bestimmten Metallions erlaubt. Dieses Verhalten scheint eine ideale Voraussetzung für katalytisch aktive Systeme zu sein.

Introduction

Catalysis of a wealth of reactions is tightly associated with transition metals coordinated to organic ligands. On the one hand, these provide the catalytic metal ion with a molecular surrounding, which allows for a balanced binding and dissociation of the substrate. On the other hand, the stereochemical nature of the ligand system is the indispensable requirement for regio- and stereoselectivity in many cases [1].

In recent communications, we described a series of novel ligands which were derived from naturally occurring linear tetrapyrroles by means of a pyridinologous substitution of pyrrolic units [2, 3]. As it turned out that the copper complexes of **1** and **2** exhibited catalytic activity in the cyclopropanation of alkenes, it seemed to be worthwhile to study the complexation behavior of these ligands in general. Following this lead, crystal structural analyses of representative examples seemed to be of fundamental interest in order to possibly correlate structural details with catalytic activity.



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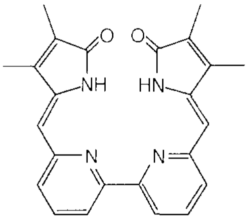

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Results and Discussion

Complexes Derived from Ligand 1

As shown in Fig. 1, the copper complex **3** involving the ligand **1** was actually found to be a dimeric system, $(\mathbf{3})_2$. This resulted in an intricate bonding pattern to provide the copper ion with its proper coordination. The copper atom was found to be penta-coordinated, resulting in a coordination polyhedron made up of a distorted rectangular pyramid. The nitrogen atoms N1 and N3 of the first subunit (with Cu–N1 and Cu–N3 distances of 1.89(1) Å) and oxygen atoms $O1^i$ and $O2^i$ of the second subunit (with $CuO1^i$ and $CuO2^i$ ($i = -x, y, 1/2 - z$) distances of 2.18(1) and 2.21(1) Å) were derived to be configured *trans* to each other and to occupy the equatorial plane, whereas the apical position was occupied by the nitrogen atom N2 (with a Cu–N2 distance of 2.13(1) Å). The copper atom was found to be displaced

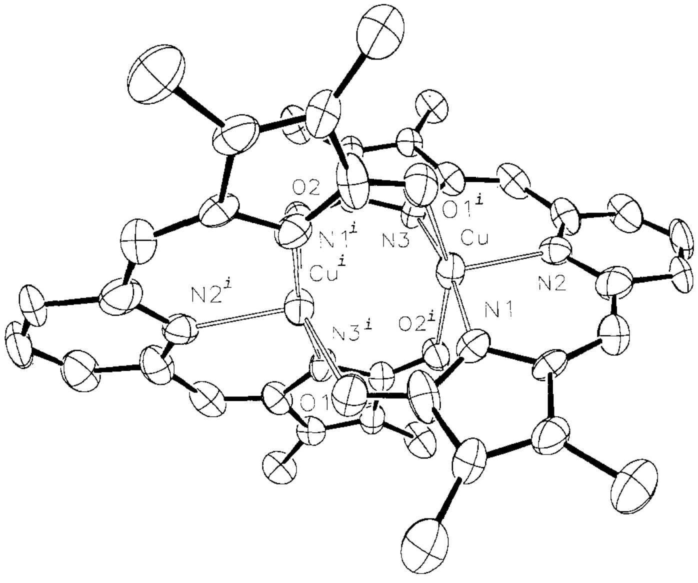


Fig. 1. ORTEP92 plot of the molecular structure of $(\mathbf{3})_2$; the solvate chloroform molecule is not shown; symmetry code: $i = -x, y, 1/-z$; the detailed atom labeling is shown in Scheme 1

by 0.253(1) Å out of the mean plane defined by the carbonyl oxygen and the nitrogen atoms $O1^i$, $O2^i$, N1, and N3. The two copper ions are placed 2.886(2) Å apart of each other.

The pyridinologous ligand **1** was observed to be in a *synperiplanar,synperiplanar* conformation with insignificant deviations from planarity. This planarity was mainly provided by a widening of the two methine bonding angles by about 9°. Accordingly, the ligand was found to be of approximate C_{2v} symmetry. According to the rather normal bond length within and between the three ring fragments (*e.g.*, C4–C5 = 1.35(2) Å and C5–C6 = 1.43(2) Å; similarly C10–C11 = 1.50(3) Å and C11–C12 = 1.37(2) Å), the ligand retained the canonical bonding features of the free ligand, *i.e.*, two methylene-lactam rings are conjugated with a pyridine ring. The two subunits in the complex were found to be arranged nearly orthogonal to each other with an interplanar angle of 84.6(3)° between two planes, each defined by the three nitrogen atoms belonging to the corresponding subunit. As illustrated in Fig. 2, the molecule of $(\mathbf{3})_2$ was associated with two molecules of chloroform to build the unit cell of the crystal.

Compared with the results from force field calculations of the free ligand **1** and its copper complex **3** [2, 3], the structure of $(\mathbf{3})_2$ came as a surprise. It has been found that in **3** the ligand had to be considerably twisted (47°) at the two exocyclic single bonds to accommodate a nonplanarely coordinating copper ion [3]. Obviously, the dimerization observed in the present case yielded a situation in which a more

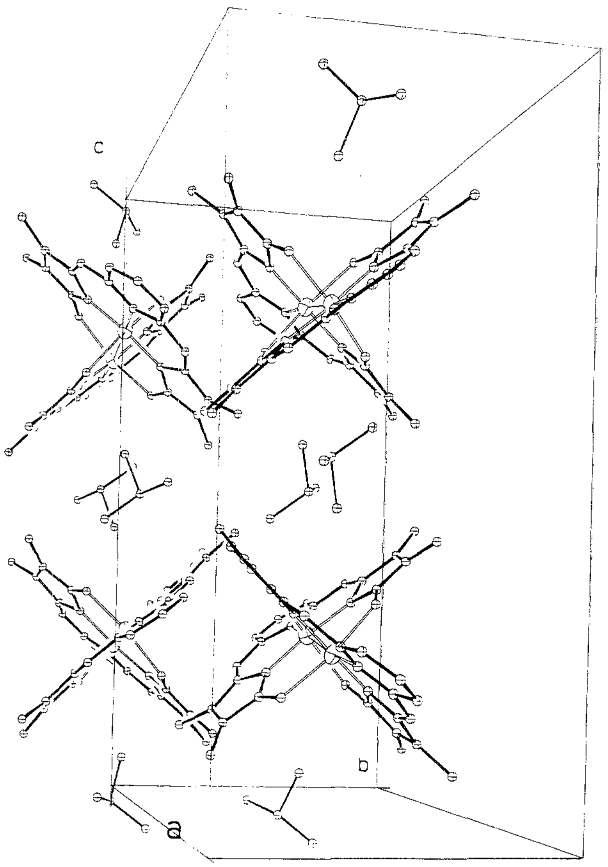


Fig. 2. Crystal structure of $(\mathbf{3})_2$

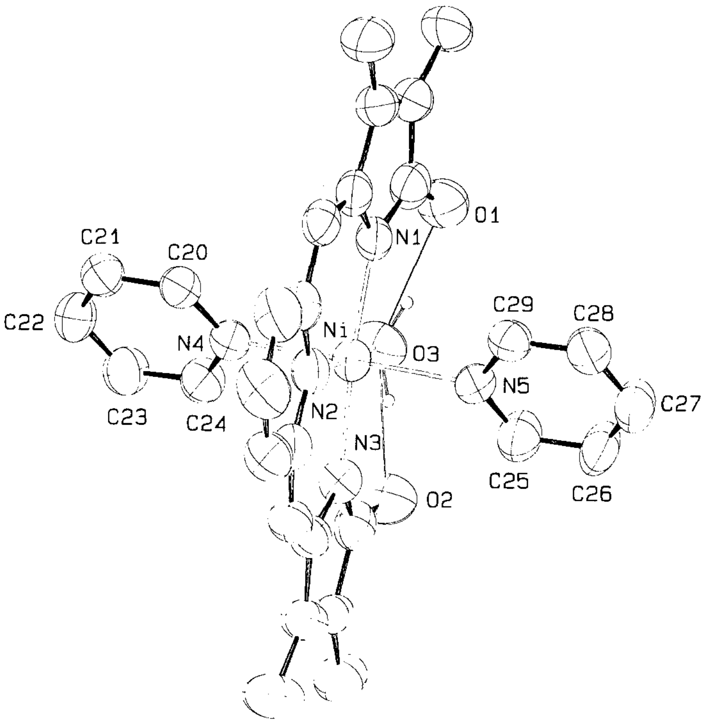


Fig. 3. ORTEP92 plot of the molecular structure of **4**; the detailed atom labeling is shown in Scheme 1

favorable coordination situation was reached at the expense of the energy needed to expand the methine bonding angles.

In contrast to the copper complex **3**, the nickel complex **4** was derived to be monomeric and the central ion to be hexa-coordinated. The crystal structure of **4** is built up of two crystallographically independent molecules and one molecule of benzene in the asymmetric unit. Both molecules are essentially identical and are discussed together: the conformational details of the first independent molecule are followed by those of the second one given in square brackets. Three coordination sites of the metal ion were filled by the nitrogen atoms of the ligand **1** (with Ni–N1, Ni–N2, and Ni–N3 bonding distances of 2.038(6), 2.170(5), and 2.027(6) Å [2.038(5), 2.148(5) and 2.048(5) Å]) as shown in Fig. 3. The ligand departed slightly but significantly from a *synperiplanar,synperiplanar* planar conformation. Similarly to the ligand geometry in $(\mathbf{3})_2$ the planarization was mostly achieved by a widening of the bond angles at the methine fragment by about 10°. At the fourth position there resided a water molecule (Ni–O3 distance 2.081(4) Å [2.059(4) Å]). The water molecule acted as a hydrogen bonding bridge between two oxygen atoms. This bridge was characterized by O3–H31···O1 and O3–H32···O2 distances of 2.569(7) [2.558(6)] and 2.584(7) Å [2.558(6) Å] and bonding angles of 166.6(4)° and 170.0(4)° [152.1(3)° and 170.6(3)°]. The two remaining coordination sites of the nickel ion were occupied by two pyridine molecules (Ni–N4 and Ni–N5 distances of 2.177(6) Å and 2.186(6) Å [2.195(6) and 2.196(6) Å]. Thus, an almost ideal octahedral complex was observed in the case of the nickel ion. No special intermolecular contacts seemed to support the arrangement of the molecules in the crystal.

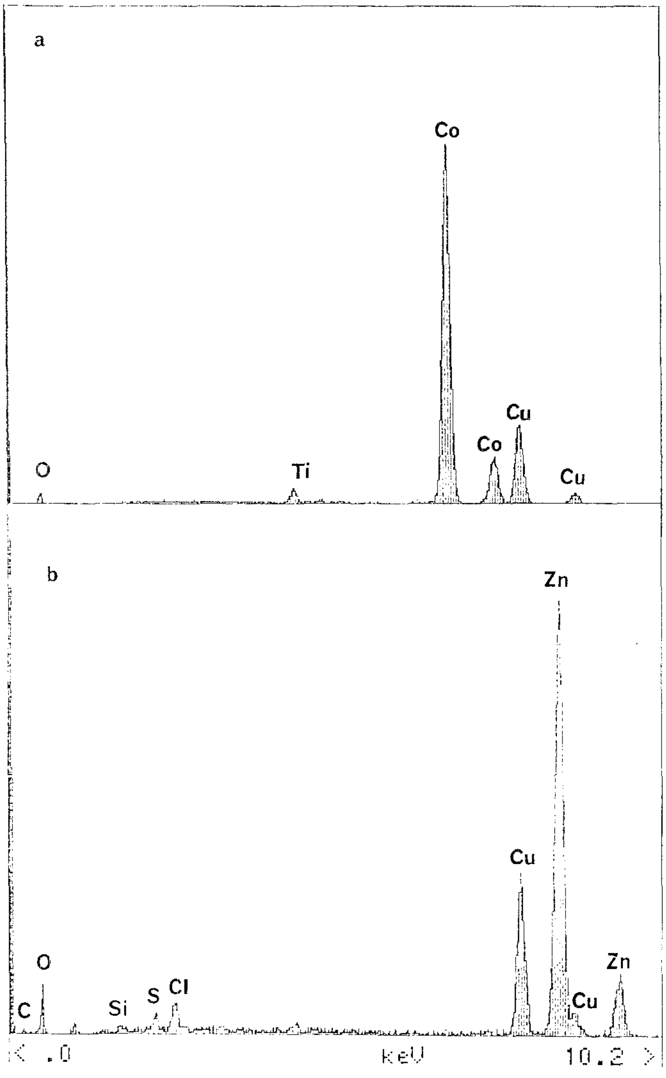


Fig. 4. Energy dispersive spectrum of **5** (a) and (**6**) (b)

The cobalt and zinc complexes of **1** (**5** and **6**) were found to be isostructural, and therefore values for the zinc complex will be given in square brackets after the values for the cobalt complex in the following discussion. To prove the existence of Co in **5** and of Zn in **6**, EDS spectra were recorded. In Fig. 4a, the energy dispersive spectrum of **5** is shown. In addition to the expected CoK_α and CoK_β lines, the lines of copper and titanium were found to be present. They result from the copper grid and sample holder materials. In Fig. 4b, the dispersive X-ray spectrum of **6** is displayed. As could be expected, the Zn$L_{\alpha 1}$, ZnK_α, ZnK_β, CK_α, and OK_α lines were observed together with the lines belonging to the grid and sample holder materials. In addition, traces of S, Si, and Cl were observed as impurities.

Figure 5 shows the main structural features of this system which provides an additional bonding motive to the coordination behavior of **1**. The metal ion (Co, Zn) was found to be penta-coordinated in a distorted trigonal bipyramid with N1, N3, and N4 in the equatorial positions and N2 and water oxygen O3 in the axial positions. Distances of Co–N1, Co–N2, Co–N3, Co–N4, and Co–O3 were found

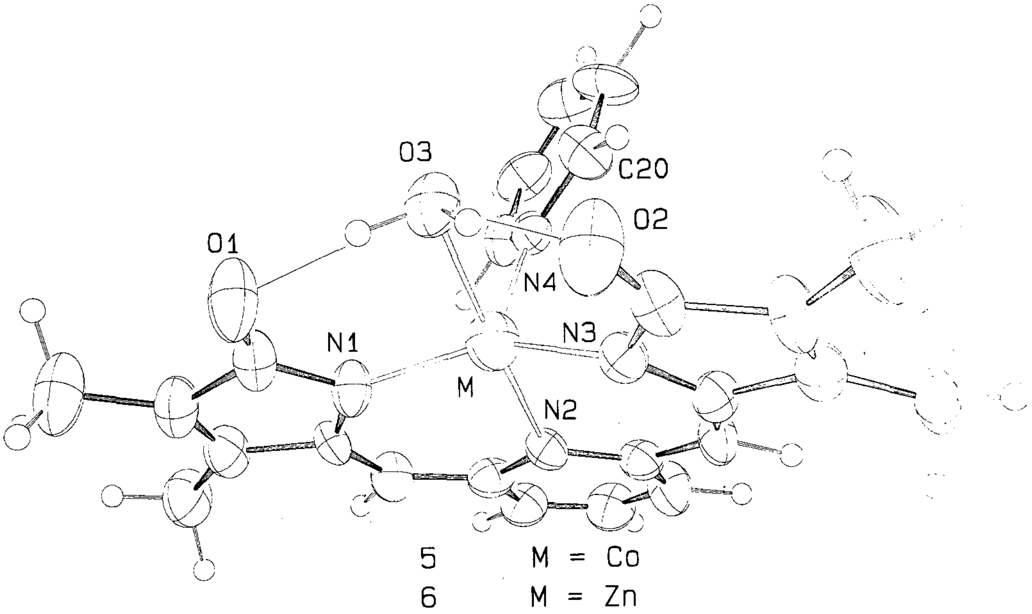


Fig. 5. ORTEP92 plot of the molecular structure of **5** and **6**; the detailed atom labeling is shown in Scheme 1

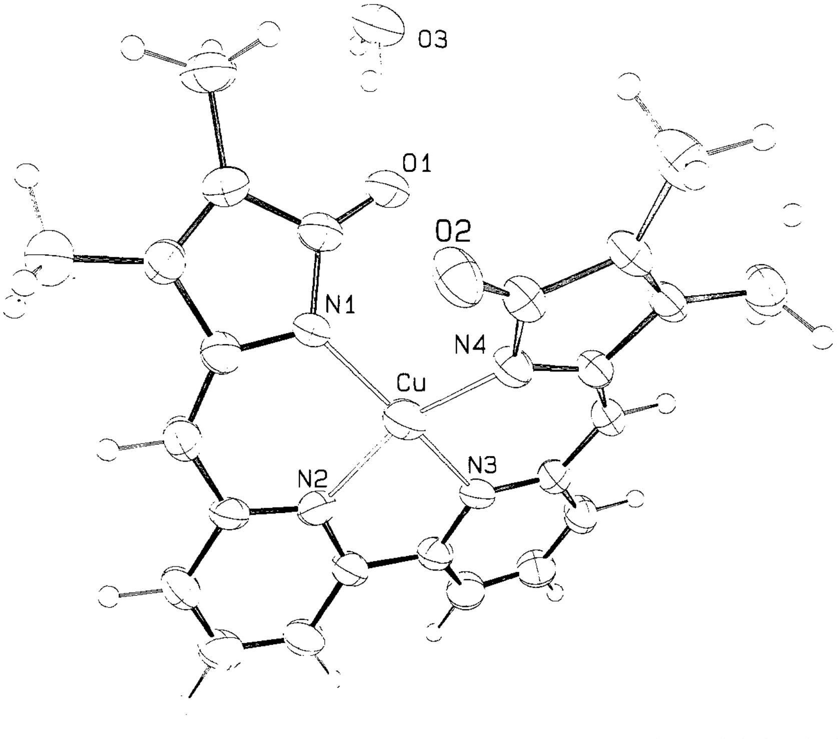


Fig. 6. ORTEP92 plot of the molecular structure of **7**; the detailed atom labeling is shown in Scheme 1

to be 2.187(7), 1.982(6), 2.092(6), and 2.185(6) Å [the corresponding Zn values were observed as 1.971(4), 2.221(4), 1.980(4), 2.113(3), and 2.280(4) Å]. The water molecule was found to be involved in the hydrogen bonds O3–H31···O1 and O3–H32···O2 which were characterized by bond lengths of 2.633(8) and 2.635(8) Å [2.652(6) and 2.632(5) Å] and bond angles of 161.0(4) and 147.4(4)° [166.7(3) and 158.3(3)°]. The ligand was derived to be in a *synperiplanar,synperiplanar* conformation which was significantly twisted. The dihedral angles at the two exocyclic double bonds (N1–C4–C5–C6 and C15–C16–C17–N4) were found to amount to 5(2) and −4(2)° [3.0(9) and −2.2(9)°]. Moreover, due to the penta-coordination the cobalt ion was displaced from the ligand's pyridine plane by −0.791(1) Å [−0.810(1) Å]. The ligating requirements of the central ion in **5** and **6** were mainly satisfied by widening the bond angles at the ligand's methine fragments by about 9° and 10°. No special intermolecular contacts were found to support the arrangement of the molecules in the crystal.

It is interesting to note that this kind of adaptive behavior of a ligand like **1** to the different requirements of the coordination centers seems to be characteristic of linear oligopyrroles [4]. For example, in the case of the zinc complex of a formylbiliverdin a water binding penta-coordinated monomer and a tetra-coordinated dimer with different conformational situations of the ligand have been observed [5].

A Complex Derived from Ligand **2**

The structural details of the copper complex **7** of ligand **2** is shown in Fig. 6. The copper ion was found to be coordinated to the four nitrogen atoms of the ligand in a distorted square plane. By twisting the ligand at the three exocyclic single bonds it was possible to accommodate it to a dihedral distorted planar coordination geometry of the copper ion (with Cu–N1, Cu–N2, Cu–N3, and Cu–N4 distances of 1.919(4), 1.990(6), 2.004(4), and 1.924(5) Å). The ligand was found to be in its *synperiplanar, synperiplanar, synperiplanar* conformation with the bipyridine fragment twisted by 16°. The two exocyclic single bonds joining it to the lactam fragments were found to be twisted by 9 and 5°. The methine fragment bond angles were widened by about 6°, thus also contributing to the relief of steric strain within the ligand.

As can be seen from the crystal structure of **7** in Fig. 7, the molecules of **7** are interconnected in the crystal by a hydrogen bonding scheme involving one molecule of water per molecule of the complex in the unit cell. Characteristic distances for O3–H31···O1 and O3–H32···$O2^i$ ($i = -1 + x, y, z$) of 2.821(7) and 2.850(6) Å and bond angles of 164.4(3) and 160.5(3)° were derived.

In conclusion, **1** and **2** were derived to constitute ligand systems for which three different kinds of coordination behavior were found. **1** uniquely allows to accommodate the specific ligand field demands of a certain central metal ion. The trend to form a dimeric system as was observed in $(\mathbf{3})_2$ seemed to be an ideal prerequisite to provide a catalytically active system. Only rather small energy differences would obviously be encountered on separating the two subunits to allow their binding to the substrate.

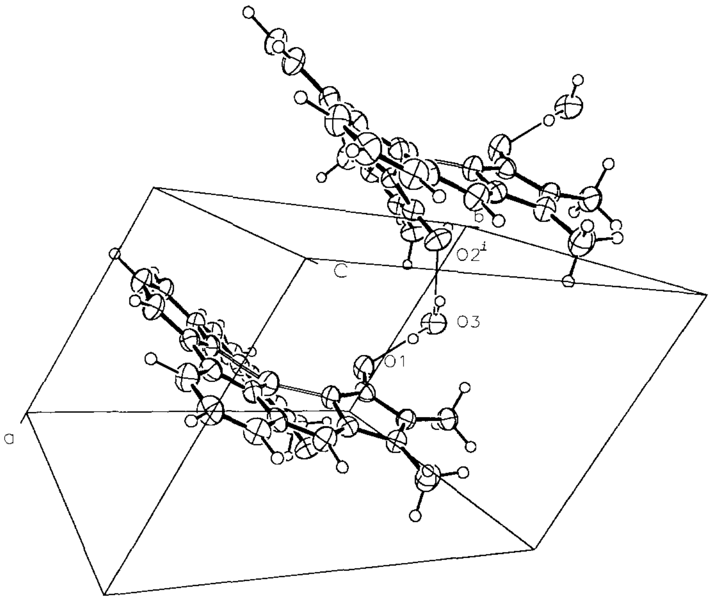
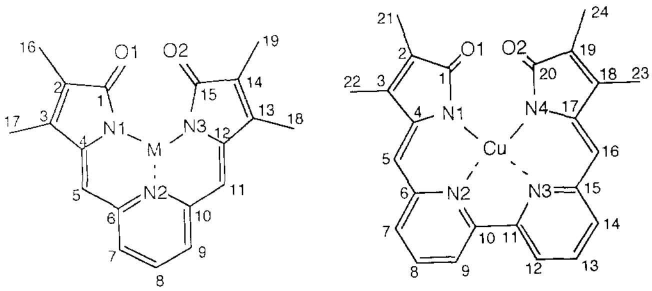


Fig. 7. Crystal structure of 7; symmetry code: $i = -1 + x, y, z$

Experimental

Melting points were taken by means of a Kofler hot stage microscope (Reichert, Vienna). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM-360 spectrometer using *DMSO*-d_6 as solvent and *TMS* as internal standard. UV/Vis and IR spectra were recorded using Perkin Elmer 297, Phillips PU 8700, and Biorad FTIR instruments. X-ray experiments were carried out using a Philips PW1100 diffractometer updated by Stoe and supported by an electron microscope. Qualitative energy dispersive X-ray analysis (EDS) was performed on a JEOL JEM 2010 200 kV electron microscope connected to a LINK-EDS system with a Si (Li) detector. Compounds **5** and **6** were powdered and suspended on a TEM carbon foil on a copper grid.

The ligands **1** and **2** and their Cu(II) complexes **3** and **7** were synthesized according to Refs. [2, 3]. The other derivatives were prepared according to the following general procedure. A solution of 0.16 mmol of the ligand in 5 ml ethanol was refluxed for 15 minutes. Then, 0.24 mmol of the solid metal acetate was added and the reaction mixture refluxed for additional 30 minutes. Upon cooling the complex crystallized and was separated by filtration.



3 M = Cu
4 M = Ni
5 M = Co
6 M = Zn

7

Scheme 1. Structures of **3**–**7** with atomic labeling; solvent ligands were omitted

3,4-Dimethyl-5-(2-(6-methyl-(3,4-dimethyl-2-oxo-3-pyrrolin-5-methylidene)-pyridyl)-methylidene)-3-pyrrolin-2-one copper(II)·chloroform (1:1) (**3**; $C_{19}H_{17}N_3O_2Cu \cdot CHCl_3$)

This complex was prepared according to Refs. [2, 3]. Crystals were obtained by means of the evaporation method from a solution in chloroform and *n*-hexane.

Aqua(pyridine)-3,4-dimethyl-5-(2-(6-methyl-(3,4-dimethyl-2-oxo-3-pyrrolin-5-methylidene)-pyridyl)-methylidene)-3-pyrrolin-2-one nickel(II)·benzene (2:1)
(**4**; $((H_2O)(C_5H_5N)C_{19}H_{17}N_3O_2Ni)_2 \cdot C_6H_6$)

Yield 82%; m.p.: not until 300°C; IR (KBr): $\nu = 2935, 1665, 1540, 1455, 1400, 1190\,cm^{-1}$; UV/Vis (pyridine): $\lambda_{max} = 315$ (28500), 385 (14400), 476 (9800), 507 (9200 nm (ε). Crystals were obtained by means of the evaporation method from a solution in pyridine and benzene.

Aqua(pyridine)-3,4-dimethyl-5-(2-(6-methyl-(3,4-dimethyl-2-oxo-3-pyrrolin-5-methylidene)-pyridyl)-methylidene)-3-pyrrolin-2-one cobalt(II) (**5**; $(H_2O)(C_5H_5N)C_{19}H_{17}N_3O_2Co$)

Yield 88%; m.p.: not until 300°C; IR (KBR): $\nu = 2925, 1665, 1540, 1455, 1400, 1190\,cm^{-1}$; UV/Vis (pyridine): $\lambda_{max} = 317$ (26900), 472 (8500) nm (ε). Crystals were obtained by means of the evaporation method from a solution in pyridine and benzene.

Aqua(pyridine)-3,4-dimethyl-5-(2-(6-methyl-(3,4-dimethyl-2-oxo-3-pyrrolin-5-methylidene)-pyridyl)-methylidene)-3-pyrrolin-2-one zinc(II)·water (1:1)
(**6**; $(H_2O)(C_5H_5N)C_{19}H_{17}N_3O_2Zn \cdot H_2O$)

Yield 83%; m.p.: not until 300°C; ^1H NMR (360 MHz, δ, *DMSO*-d$_6$): 1.82 (s, 6H), 2.05 (s, 6H), 5.91 (s, 2H), 7.28 (d, $J = 8$ Hz, 2H), 7.81 (t, $J = 8$ Hz, 1H) ppm; ^{13}C NMR (50 MHz, δ, *DMSO*-d$_6$): 8.1, 8.2, 9.6, 99.8, 123.2, 131.0, 137.2, 139.1, 141.9, 153.1, 155.1 ppm; IR (KBr): $\nu = 2914, 1660, 1601, 1536, 1446, 1384, 1165, 1112\,cm^{-1}$; UV/Vis (ethanol): $\lambda_{max} = 311$ (33400), 447 (12200), 475 (10100) nm (ε). Crystals were obtained by means of the evaporation method from a solution in pyridine and benzene.

6,6'-bis-(3,4-Dimethyl-2-oxo-3-pyrrolin-5-methylidene)-methyl-2,2'-bipyridyl copper(II)·water (1:1)
(**7**; $C_{24}H_{20}N_4O_2Cu \cdot H_2O$)

This complex was prepared according to Refs. [2, 3]. Crystals were obtained by means of the evaporation method from a solution in chloroform and *n*-hexane.

X-ray data collection, reduction, and structure refinement

Details concerning the measurements and refinements are presented in Table 1a, and the crystal data of **3**–**7** in Table 1b. Data collection and reduction were controlled by the Stoe program package [6]. Corrections for *Lorentz* and polarization were applied for all five structures. Extinction correction was applied for **4**, **6**, and **7**. The structures of **4**–**7** were solved by direct methods using the SIR-88 program [8]. Positional and anisotropic parameters for all non-hydrogen atoms were refined using the weighting scheme for **3**, **4**, **6**, and **7**. Several hydrogen atoms were located in difference *Fourier* maps (34 in **4**, 19 in **5**, 17 in **6**, and 17 in **7**), but their bond lengths were recalculated to their theoretical values and constrained. For **3**, the hydrogen atom positions could be calculated. Final atomic and equivalent isotropic thermal parameters were calculated according to $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. ORTEP92 plots [9] with appropriate labeling are displayed in Figs. 1, 3, and 6 for compounds **3**, **4**, and **7**, and

Table 1a. Details concerning the measurements and refinement for structures **3–7**

Compound	**3**	**4**	**5**	**6**	**7**
Unit cell determination					
Wave length (graphite monochromated)	*MoKα*	*CuKα*	*MoKα*	*CuKα*	*CuKα*
Number of reflections	9	19	20	26	24
2Θ range (°)	13.6–20.8	19.1–46.1	16.2–25.7	26.0–39.7	24.8–39.8
Data collection and reduction					
Scan mode	ω	ω	ω	ω	ω
Scan rate, scan width	variable	variable	variable	variable	variable
Intensity variation (%)	7.8	9.8	5.1	15.02	11.5
Number of standard reflections	3	2	2	3	3
2Θ range (°)	4.0–60.0	6.0–127.0	4.2–60.0	6.1–127.0	7.4–127.0
Max. h, k, l:	23, 16, 32	20, 23, 21	13, 20, 22	11, 16, 18	8, 14, 14
Number of measured reflections	6575	9716	6930	3807	3556
Number of unique reflections	5941	9398	6479	3635	3426
R(int)	0.000	0.000	0.153	0.000	0.047
Refinement performed on F^2 full-matrix least-squares by SHELXL-93 [11]					
Number of refined parameters	262	740	289	290	290
Number of observed reflections, $F_0 > 4\sigma(F_0)$	935	4333	1284	2660	2407
R	0.046	0.056	0.043	0.053	0.055
S	0.931	0.785	0.902	1.022	0.992
w	0.0950, 15.8771	0.1226, 7.6450	0.1000, 0.000	0.1017, 2.0957	0.0970, 1.0261
$wR(F^2)$ for all data	0.298	0.192	0.241	0.164	0.156
$(\Delta/\sigma)_{\max}$	0.338	−0.483	−0.029	0.348	0.040
Difference map residua (eÅ^{-3})	0.41, −0.45	0.44, −0.40	0.27, −0.27	0.50, −0.79	0.60, −0.58

Table 1b. Crystal data for structures 3–7

Compound	**3**	**4**	**5**	**6**	**7**
M_r	502.3	593.3	475.4	481.9	478.0
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P\mathrm{bcn}$	$P2_1/\mathrm{a}$	$P2_1/\mathrm{n}$	$P2_1/\mathrm{n}$	$P\bar{1}$
a(Å)	16.254(4)	16.848(1)	9.623(3)	9.643(1)	7.555(4)
b(Å)	11.038(2)	19.871(9)	14.513(4)	14.505(1)	12.253(7)
c(Å)	22.544(9)	18.152(5)	16.070(5)	16.163(2)	12.634(7)
α(°)	90	90	90	90	105.57(3)
β(°)	90	109.78(1)	99.54(3)	99.55(1)	97.12(3)
γ(°)	90	90	90	90	107.59(3)
V(Å^3)	4045(2)	5719(3)	2213(1)	2229.4(4)	1047(1)
Z	8	4	4	4	2
D_m(Mgm^{-3})	1.607	1.349	1.458	1.440	1.482
D_c(Mgm^{-3})	1.650	1.378	1.427	1.435	1.516
Crystal dimensions (mm)	0.23 × 0.16 × 0.21	0.36 × 0.46 × 0.42	0.21 × 0.05 × 0.35	0.41 × 0.38 × 0.63	0.38 × 0.15 × 0.06
Crystal colour	light brown	dark brown	dark red–brown	dark orange	dark red–brown
μ(mm^{-1})	1.50	1.28	0.80	0.18	1.77
F(000)	2056	2488	988	1000	494

in Fig. 5 for compounds **5** and **6**. Packing diagrams of **3** and **7** are presented in Figs. 2 and 7. The structural geometries* were analyzed by means of the CSU program [10].

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* Additional material to the structure determinations may be ordered from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, Federal Republic of Germany, referring to the deposition number CSD-58830, the names of the authors and the citation of the present paper.