

Pyridazine-Based Ligands and Their Coordinating Ability towards First-Row Transition Metals

Katrin R. Grünwald,^[a] Gerald Saischek,^[a] Manuel Volpe,^[a] Ferdinand Belaj,^[a] and Nadia C. Mösch-Zanetti*^[a]

Keywords: Nitrogen heterocycles / Schiff bases / Tridentate ligands / Chelates

Tridentate pyridazine ligands with two different substituents at the 3- and 6-positions (pyridyl hydrazone at the 3-position and tolyl **3**^{tol} or *tert*-butyl **3**^{tBu} at the 6-position) were prepared in high yields from 3,6-disubstituted pyridazine hydrazines and pyridine aldehyde by Schiff base condensation. This provides a facile entry into a novel class of heterocyclic molecules exhibiting interesting coordinating abilities. They react with first-row transition metal nitrates to yield complexes of the type [ML₂](NO₃)₂ (L = **3**^{tol}; M = Co **4**, M = Ni **5**, M = Zn **7**) and [ML(NO₃)₂] (L = **3**^{tol}, M = Cu **6**; L = **3**^{tBu}, M = Ni **8**, M = Cu **9**, M = Zn **10**) as crystalline solids. With the exception of copper compound **6** all complexes employing ligand **3**^{tol} form complexes of the ML₂ type, whereas with ligand **3**^{tBu} exclusively complexes of the ML type are formed,

which demonstrates the influence of the substituent at the 6-position despite its being located far from the coordination site. This points to a pronounced electronic effect. Molecular structures of all complexes were determined by single-crystal X-ray diffraction analysis revealing six-coordinate metal centers in a N₆ coordination sphere consisting of two ligands **3** or in a N₃O₃ sphere with one ligand and two nitrates in the O₂- and O,O'-coordination modes, respectively. Diamagnetic zinc complexes **7** and **10** were characterized in solution by ¹H NMR spectroscopy. All other complexes are paramagnetic (Evans' method). The redox behavior of all complexes was investigated by cyclic voltammetry, which revealed that the complexes possess the same stoichiometry in solution and in the solid state.

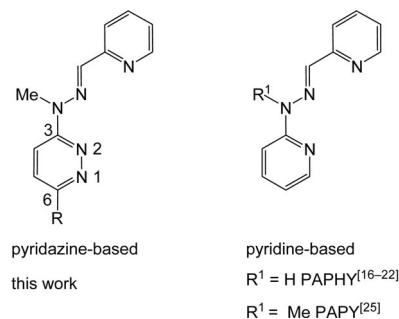
Introduction

Substituted pyridazine-based compounds are extensively investigated with regard to their versatile applications. Pyridazines interfere in regulation processes of various enzymes and find wide application in drug design.^[1–3] Analogously, agricultural science takes advantage of their high biological activity, and pyridazines whose substitution patterns have been modified display powerful fungicide properties.^[4–6] Furthermore, simple pyridazines rate high as halogen-free flame retardants.^[7]

Pyridazines have also been used as ligands in coordination chemistry. The electron-deficient aromatic system containing two nitrogen atoms leads to decreased electron-donor abilities in comparison to pyridines, which is reflected by significantly lower p*K*_a values (2.24 for parent pyridazine vs. 5.25 for pyridine).^[8] The two vicinal nitrogen donor atoms in the pyridazine heterocycle allow, in principle, the coordination of two metal centers in close proximity. However, in nonmacrocyclic ligands, two additional donor sites attached to the aromatic ring on both sides of the nitrogen

atoms (3,6-positions) or secondary bridging ligands seem to be a prerequisite to accommodate two or more metal atoms in elaborate structures.^[9–13] Thus, pyridazines without adjacent coordination sites act mostly as monodentate ligands comparable to pyridine.^[14,15]

Pyridazines with only one additional donor next to a ring nitrogen atom, leading to bi- or tridentate ligands, have been significantly less investigated in coordination chemistry, despite the unique electronic situation imposed by the pyridazine ring. Here, we report on the preparation of pyridazine-based ligands that contain additional donor sites at the 3-position of the heterocycle, whereas the 6-position is substituted by a noncoordinating aryl or alkyl group.



[a] Institut für Chemie, Bereich Anorganische Chemie, Karl-Franzens-Universität Graz, Schubertstrasse 1, 8010 Graz, Austria
Fax: +43-316-380-9835
E-mail: nadia.moesch@uni-graz.at

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejic.201000120>.

Structurally, the ligands described here bear resemblance to a pyridine-based ligand, which is widely known as PAPHY (pyridine-2-aldehyde-2-pyridylhydrazone) but is

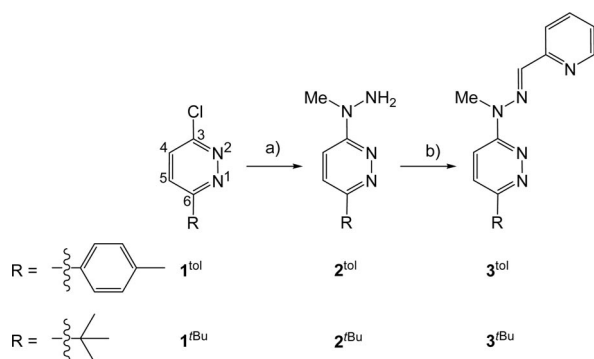
expected to exhibit significantly different electronic features. PAPHY was first described in 1957^[16] and subsequently extensively studied.^[17–22] Throughout the literature two types of complexes, namely the mono^[23] and the bis complex^[24] can be found for this ligand type, depending on the donor ability of the counterion. The observed poor stabilities in solution and the easy deprotonation of the hydrogen atom at the hydrazone backbone represent the major drawbacks in PAPHY complexes, as the pH value must be kept within small ranges. Methylation of the nitrogen atom seemed to be a viable solution without changing the spectroscopic properties of the complexes.^[25] These methylated derivatives recently experienced a renaissance as the key building blocks in forming self-assembled morphologies. Complex grid- and rack-type constructions^[26–28] are induced by dynamic structural and conformational changes of the ligand backbone as described by Lehn and co-workers.^[29–31] Similar research with pyridazine-based ligands was not pursued, which is certainly due to the as yet elusive pyridazine building blocks.

In this work, we describe a series of first-row transition metal complexes with novel pyridazine ligands. Fine tuning in the ligand backbone provides us with a simple tool to direct complex stoichiometry. Molecular structures were determined by X-ray diffraction, and electrochemical behavior in solution was investigated by cyclic voltammetry.

Results and Discussion

Synthesis of the Ligands

Two new pyridazine-based ligands were prepared starting from 3-chloro-pyridazine according to Scheme 1. The latter can be synthesized in a three-step procedure as described in the literature.^[32,33] Subsequent reaction with methyl hydrazine in ethanol at refluxing temperature afforded **2**^{tol} and **2**^{tBu} in high isolated yields with high purities. NMR spectroscopy on crude samples shows the selective substitution at the 1-position of methyl hydrazine. Schiff base condensation with 2-pyridine aldehyde in ethanol gave the ligands

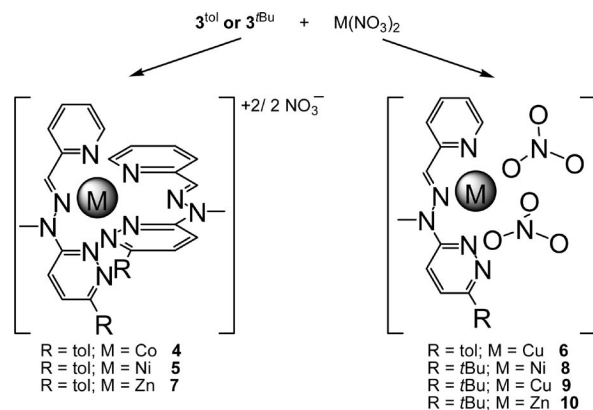


Scheme 1. Synthesis of ligands **3**^{tol} and **3**^{tBu} with two different substituents at the 6-position starting from the corresponding 3-chloropyridazine: (a) 1 equiv. methyl hydrazine in EtOH, reflux, 10 h; (b) 1 equiv. 2-pyridine aldehyde in EtOH (3 drops of acetic acid), reflux, 45 min.

3^{tol} and **3**^{tBu} in quantitative yields. The tolyl-substituted ligand is obtained as a white crystalline solid and the *t*Bu derivative as a light yellow solid. They are characterized by spectroscopic methods. Imine formation is indicated by the absence of the NH₂ signal (at ca. 4 ppm) and the appearance of the imine resonance (singlet at δ = 7.83 ppm) in the ¹H NMR spectra. The resonances assignable to the other protons in the molecules are barely influenced by the substitution. Both represent a completely novel type of ligand. (NMR spectra are available as Supporting Information).

Synthesis of the Complexes

The coordination ability of the synthesized ligands towards some first-row transition metals was investigated. Syntheses of the complexes were inspired by literature procedures.^[37,38] Solutions of **3**^{tol} or **3**^{tBu} in ethanol were refluxed, which was followed by the addition of M(NO₃)₂ (M = Co, Ni, Cu, Zn) as a 0.1 M solution in ethanol. Coordination was immediate, as a change of color was apparent. The solutions were heated at reflux for an additional 20 min to ensure completeness of the reaction. Most compounds were obtained as air-stable crystalline solids upon cooling. Some crystallized after the addition of diethyl ether to the ethanol solution as indicated in the Experimental Section. For all complexes, we were able to obtain crystals suitable for X-ray diffraction analysis (vide infra), revealing the formation of 1:1 or 1:2 complexes depending on the substituent at the 6-position of the pyridazine ring as shown in Scheme 2.



Scheme 2. Formation of 1:1 and 1:2 complexes.

All complexes with ligand **3**^{tBu} form 1:1 complexes (**8**, **9**, and **10**), whereas with **3**^{tol} both 1:1 (**6**) as well as 1:2 complexes (**4**, **5**, and **7**) are formed. In complexes of the 1:1 type, one η^1 - and one η^2 -nitrate ion complete the six-coordinate coordination site. The ligand-to-metal ratio observed within the complexes is independent of the molar ratio applied in the reaction mixture. It seems unlikely that only the larger steric demand of the *tert*-butyl group prevents coordination of a second ligand, since it is located at the 6-position pointing away from the metal site. Presumably, a combination of the steric bulk and the electron-releasing effect of *t*Bu, which leads to a higher electron donating capability, prevents substitution of nitrate.

All complexes are air-stable crystalline solids. Compounds **4**, **5**, **6**, and **7** are very poorly soluble in water and acetone, moderately soluble in acetonitrile and alcohols, and fairly well soluble in dimethyl sulfoxide, but still not well enough to obtain a meaningful ^{13}C NMR spectrum even after measurement overnight. Complexes **8**, **9**, and **10** are just slightly more soluble in dmsol, alcohols, acetonitrile, and acetone due to the *t*Bu moiety; however, concentrations sufficient for measuring a ^{13}C NMR spectrum could not be obtained, either. All complexes are completely insoluble in dichloromethane and ethers. For this reason, all spectroscopic and susceptibility data were obtained in dmsol, this being the only solvent capable of achieving sufficiently high concentrations. Electrochemical measurements (*vide infra*), however, could be carried out in dry acetonitrile.

The proton NMR spectra of the diamagnetic zinc complexes **7** and **10** in $[\text{D}_6]\text{dmsol}$ show in both cases one resonance set for the ligands, confirming the equivalency of both coordinated ligands in complex **7** and also confirming the structures revealed by X-ray crystallography. The spectrum of **7** additionally contains resonances for ethanol, which could not be removed by extensive drying under high vacuum for 96 h. The chemical shifts of the coordinated ligand resonances are only slightly different from those of the free ligands, so NMR spectroscopy is not a suitable tool to confirm coordination in solution for the diamagnetic complexes. The paramagnetism of the cobalt (**4**), nickel (**5** and **8**), and copper (**6** and **9**) complexes prevented the determination of the structure by NMR spectroscopy. However, their magnetism in solution could be determined by Evans' method,^[34] and the results are given in Table 1 along with the theoretically expected number of unpaired electrons assuming the complexes to be octahedral high-spin species.

Table 1. Unpaired electrons determined by the Evans' method.

	$\mu_{\text{obsd.}}/\text{BM}$	Unpaired e^-	Unpaired e^- (theor.)
$[\text{Co}(\mathbf{3}^{\text{tol}})_2](\text{NO}_3)_2$ (4)	2.97	2.13	3
$[\text{Ni}(\mathbf{3}^{\text{tol}})_2](\text{NO}_3)_2$ (5)	2.84	2.01	2
$[\text{Cu}(\mathbf{3}^{\text{tol}})(\text{NO}_3)_2]$ (6)	1.54	0.83	1
$[\text{Ni}(\mathbf{3}^{\text{Bu}})(\text{NO}_3)_2]$ (8)	2.98	2.15	2
$[\text{Cu}(\mathbf{3}^{\text{Bu}})(\text{NO}_3)_2]$ (9)	1.58	0.87	1

With the exception of the cobalt complex, the experimental and theoretical numbers agree fairly well. The low number of unpaired electrons in the case of the cobalt complex points to a significant contribution of the low-spin species in solution and shows the ligand to be of medium strong character.^[8,39] Notwithstanding the paramagnetic character of the reported complexes, no meaningful EPR spectra (solution or solid state) could be acquired, the spectrum itself consisting generally of a single, broad, unresolved wave.

Solid State Structures of the Complexes

The molecular structures of all complexes were determined by X-ray diffraction analysis. Suitable single crystals were obtained by crystallization procedures indicated in the

Experimental Section. Molecular views including atom-numbering schemes of complexes **5**, **8** and **9** are given in Figures 1 and 2. Views of all other compounds can be found in the Supporting Information (Figures S1–S4). Crystallographic data and refinement parameters are given in Table 2, and selected bond lengths and angles of all complexes are given in Tables 3 and 4. In the following paragraphs, the two types of complexes (with ligand-to-metal ratios of 2:1 and 1:1) are described.

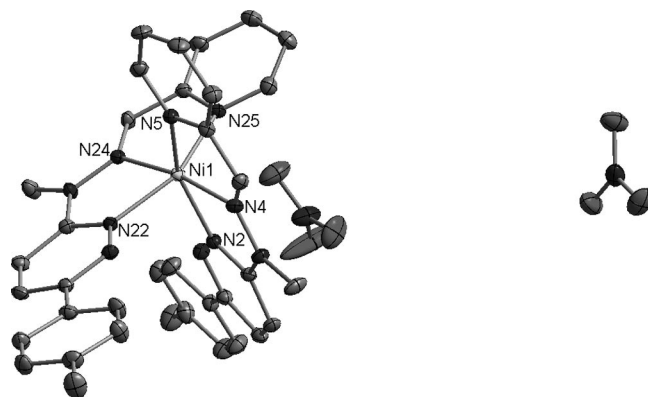


Figure 1. Molecular view of complex **5** (50% probability). Hydrogen atoms and solvent molecules have been omitted for clarity.

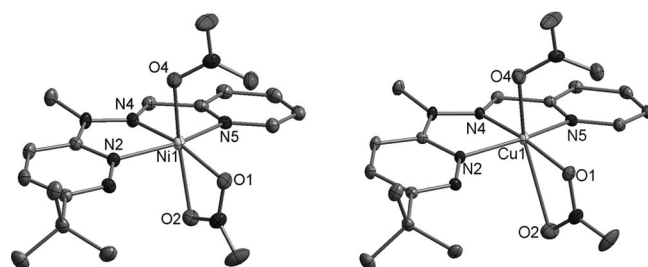


Figure 2. Molecular view of complex **8** and **9** (50% probability). Hydrogen atoms have been omitted for clarity.

Molecular Structure of Complexes **4**, **5**, and **7** (Ligand/Metal = 2:1)

Complexes **4**, **5**, and **7** are isostructural. They all contain two equivalents of ligand $\mathbf{3}^{\text{tol}}$, which coordinates in a tridentate fashion to form distorted octahedral cations. Both nitrate counterions are not coordinated to the metal center. A representative molecular view of compound **5** including the atom numbering scheme is shown in Figure 1. The distortion from ideal octahedral geometry is evident from, for example, the values of the following angles: N2-M-N5 $158.99(8)^\circ$ ($\text{M} = \text{Co}$, **4**), $155.12(12)^\circ$ ($\text{M} = \text{Ni}$, **5**), or $148.25(7)^\circ$ ($\text{M} = \text{Zn}$, **7**) or the angles N2-M-N24 $173.46(12)^\circ$ ($\text{M} = \text{Co}$, **4**), $170.10(12)^\circ$ ($\text{M} = \text{Ni}$, **5**) or $164.19(10)^\circ$ ($\text{M} = \text{Zn}$, **7**). Metal-to-nitrogen bond lengths to the pyridine and the pyridazine N atoms are in the same

Table 2. Crystallographic data and structure refinement for complexes **4–10**.

	4	5	6	7	8	9	10
Empirical formula	Co ₂ C ₇₆ N ₂₄ H ₈₀ O ₁₄	NiC ₃₈ N ₁₂ H ₄₀ O ₇	CuC ₁₈ N ₇ H ₁₇ O ₆	ZnC ₃₈ N ₁₂ H ₄₀ O ₇	NiC ₁₅ N ₇ H ₁₉ O ₆	CuC ₁₅ N ₇ H ₁₉ O ₆	ZnC ₁₅ N ₇ H ₁₉ O ₆
<i>M_r</i> / g mol ^{−1}	1671.50	835.53	490.94	842.19	452.08	456.91	458.74
Crystal description	needle, red	column, red	block, green	block, yellow	tablet, gold	tablet, green	plate, colorless
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>C2/c</i>	<i>P2₁/c</i>	<i>P1</i>	<i>C2/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> / Å	15.7497(7)	15.7949(10)	11.635(3)	15.6375(6)	14.1108(5)	13.7491(4)	13.9955(6)
<i>b</i> / Å	24.4139(10)	24.5127(15)	11.824(3)	24.9838(10)	7.6035(3)	7.5464(2)	7.6897(3)
<i>c</i> / Å	20.6835(8)	20.7312(11)	15.185(4)	20.6616(9)	17.2073(6)	17.5964(5)	17.3050(7)
<i>α</i> / °	90.00	90.00	93.12(2)	90.00	90.00	90.00	90.00
<i>β</i> / °	104.506(2)	105.816(2)	102.81(2)	104.079(2)	90.0980(10)	91.7710(10)	90.124(2)
<i>γ</i> / °	90.00	90.00	92.74(2)	90.00	90.00	90.00	90.00
Volume / Å ³	7699.5(6)	7722.7(8)	2030.2(9)	7829.7(6)	1846.19(12)	1824.86(9)	1862.38(13)
<i>Z</i>	4	8	4	8	4	4	4
<i>T</i> / K	100(2)	100(2)	95	100(2)	100(2)	100(2)	100(2)
<i>D_c</i> / g cm ^{−3}	1.442	1.437	1.606	1.429	1.626	1.663	1.636
<i>μ</i> (Mo- <i>K_α</i>) / mm ^{−1}	0.513	0.569	1.129	0.693	1.102	1.249	1.370
<i>R</i> (000)	3480	3488	1004	3504	936	940	944
Reflections collected	51924	118725	8705	84110	35823	23761	42945
Unique reflections	7574	17782	7956	7558	3855	4402	5832
Reflections with <i>I</i> ≥ 2 σ (<i>I</i>)	6300	13549	6528	6593	3513	4034	4844
<i>R</i> (int), <i>R</i> (σ)	0.0453, 0.0302	0.0443, 0.0381	0.0334, 0.0634	0.0389, 0.0231	0.0329, 0.0164	0.0292, 0.0204	0.0271, 0.0148
Number of param./restraints	530/1	1058/0	591/0	602/34	266/0	266/0	266/0
Final <i>R</i> ₁ , ^[a] <i>wR</i> ₂ ^[b] (<i>I</i> ≥ 2 σ)	0.0439, 0.1125	0.0607, 0.1423	0.0411, 0.0853	0.0385, 0.0815	0.0216, 0.0524	0.0238, 0.0613	0.0217, 0.0570
<i>R</i> indices (all data)	0.0560, 0.1203	0.0873, 0.1578	0.0551, 0.0918	0.0469, 0.0845	0.0249, 0.0543	0.0272, 0.0632	0.0263, 0.0605
GOF on <i>F</i> ²	1.058	1.186	1.034	1.146	0.999	1.035	1.048
Larg. diff. peak and hole / e Å ^{−3}	0.866, −0.734	0.825, −0.617	0.354, −0.354	0.506, −0.339	0.301, −0.279	0.468, −0.403	0.490, −0.274

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Table 3. Selected bond lengths in Å and angles in ° of compounds **4**, **5**, and **7**.

	4 (M = Co) ^[a,b]	5 (M = Ni) ^[a]	7 (M = Zn) ^[a]
M–N2	1.999(2)	2.053(3)	2.135(2)
M–N4	1.900(2)	2.004(3)	2.129 (2)
M–N5	2.066(2)	2.091(3)	2.133 (2)
M–N22	1.999(2) ^a	2.055(3)	2.135(2)
M–N24	1.900(2) ^a	2.001(3)	2.129 (2)
M–N25	2.066(2) ^a	2.085(3)	2.133 (2)
N2–M–N4	79.76(8)	76.99(12)	73.17(7)
N2–M–N5	158.99(8)	155.12(12)	148.25(7)
N2–M–N22	92.31(11)	91.89(12)	91.51(10)
N2–M–N24	95.67(8)	95.85(12)	95.61(7)
N2–M–N25	93.86(8)	94.84(12)	97.55(7)
N4–M–N5	79.66(8)	78.44(12)	75.69(7)
N4–M–N22	95.67(8)	96.30(12)	95.61(7)
N4–M–N24	173.46(12)	170.10(12)	164.19(10)
N4–M–N25	105.18(8)	108.67(12)	116.14(7)
N5–M–N22	93.86(8)	94.63(12)	97.55(7)
N5–M–N24	105.18(8)	109.01(12)	116.14(7)
N5–M–N25	87.49(12)	89.32(12)	90.57(10)
N22–M–N24	79.76(8)	76.91(12)	73.17(7)
N22–M–N25	158.99(8)	155.00(12)	148.25(7)
N24–M–N25	79.66(8)	78.46(12)	75.69(7)

[a] Data of only one molecule of the two found in the asymmetric unit are given. [b] Second ligand molecule generated by symmetry operation (N2ⁱ, N4ⁱ and N5ⁱ are represented by N22, N24 and N25).

range [from 1.999(2) Å to 2.135(2) Å] and are similar to those found in the literature for pyridine and pyridazine metal bonds.^[24,40–43] All M–N4 bond lengths are the shortest in all complexes, which was also observed for complexes of PAPHY and analogues.^[28,44]

Table 4. Selected bond lengths in Å and angles in ° of compounds **6**, **8**, **9**, and **10**.

	6 (M = Cu) ^[a]	8 (M = Ni) ^[a]	9 (M = Cu)	10 (M = Zn)
M–N2	1.967(2)	2.056(1)	1.997 (1)	2.116(1)
M–N4	1.960(2)	2.008(1)	1.962(1)	2.138(1)
M–N5	1.989(2)	2.087 (1)	2.019(1)	2.125(1)
M–O1	1.965(2)	2.062(1)	1.954(1)	2.023(1)
M–O2	2.636(2)	2.154(1)	2.678(1)	2.460(1)
M–O4	2.239(2)	2.030(1)	2.215(1)	2.036(1)
N2–M–N4	79.19(10)	76.95(4)	78.30(5)	72.89(3)
N2–M–N5	157.77(10)	154.94(4)	156.32(5)	146.19(4)
N2–M–O1	97.97(9)	101.31(4)	102.60(4)	104.47(4)
N2–M–O2	83.77(10)	89.54(4)	91.20(5)	86.11(3)
N2–M–O4	92.80(9)	86.77(4)	84.82(4)	88.32(4)
N4–M–N5	80.85(10)	78.66(4)	79.99(5)	75.35(3)
N4–M–O1	174.11(9)	167.46(4)	169.75(5)	158.79(4)
N4–M–O2	120.43(10)	106.21(4)	116.64(5)	102.12(3)
N4–M–O4	97.30(9)	91.29(4)	96.98(5)	98.18(4)
N5–M–O1	100.98(9)	101.25(4)	97.11(4)	100.87(3)
N5–M–O2	98.09(10)	91.82(4)	90.14(5)	89.46(3)
N5–M–O4	99.37(9)	99.46(4)	107.19(4)	107.53(4)
O1–M–O2	53.87(10)	61.25(4)	53.30(5)	56.73(3)
O1–M–O4	87.96(8)	101.05(4)	93.27(4)	102.80(4)
O2–M–O4	140.43(10)	160.80(4)	144.61(5)	156.30(3)

[a] Data for only one molecule of the two found in the asymmetric unit are given.

Crystal Structures of Complexes **6**, **8**, **9**, and **10** (Ligand/Metal = 1:1)

All four complexes **6**, **8–10** are isostructural. The central metal atom is coordinated by the three nitrogen atoms of one ligand molecule (**3**^{tol} in the case of copper complex **6** and **3**^{tBu} in **8–10**) as well as by the oxygen atoms of one

O- and one slipped *O,O'*-coordinated nitrate ion forming distorted octahedral geometries. The M–O bond lengths in the *O,O'*-coordinate NO₃ ion differ significantly with the oxygen occupying the apical position and increase as follows: 2.154(1) Å (**8**) < 2.460(1) Å (**10**) < 2.636(2) Å (**6**) < 2.678(1) Å (**9**). Thus, only the nickel compound **8** shows octahedral geometry. Compounds **6**, **9**, and **10** are better described as exhibiting square pyramidal geometries. Representative molecular views of the two extremes, compounds **8** and **9**, are shown in Figure 2. In the d⁹ Cu^{II} complexes **6** and **9**, tetragonal distortion of the octahedron stabilizes the system due to the Jahn–Teller effect.^[45] The three N atoms of the tridentate pyridazine ligands N2, N4, and N5 and O1 of the *O,O'*-coordinate nitrate ions form distorted square planes about the metal centers with torsion angles of –1.14(5)° (**9**), –3.41(4)° (**10**), 3.32(4)° (**8**) and –4.11(10)° (**6**). A distorted pyramidal arrangement is manifested by N2–M–O4 and N4–M–O4 angles of 92.80(9) and 97.30(9)° (**6**), 86.77(4) and 91.29(4)° (**8**), 84.82(4) and 96.98(5)° (**9**), and 88.32(4) and 98.18(4)° (**10**). The metal–oxygen distances range from 1.954(1) to 2.062(1) Å for O1 and from 2.030(1) to 2.239(2) Å for O4, where Cu–O1 distances in the two copper complexes (**6** and **9**) are slightly shorter than those in the nickel (**8**) and zinc complexes (**10**). In contrast, the Cu–O4 distances are significantly longer than Ni–O4 and Zn–O4 distances consistent to the preferred square-planar geometry typical for Jahn–Teller-distorted Cu^{II} ions. Metal–nitrogen distances range in all complexes from 1.960(2) to 2.138(1) Å, increasing from the imino-N via the pyridazine-N through to the pyridine-N bond. The coordinated nitrate ions feature oxygen–metal–oxygen angles of 53.30° (**9**), 53.87° (**6**), 56.73° (**10**), and 61.25° (**8**), which are similar to values reported in the literature.^[46]

Ligand exchange reactions employing metal halide or pseudo-halide precursors are known to lead preferably to complexes of the type metal/ligand = 1:1,^[19–22] whereas employing precursors with noncoordinating counterions leads to complexes of the type 2:1.^[18,24–26] Nitrate precursors seem to exhibit reactivity at the borderline, enabling both stoichiometries. Thus, fine-tuning of electronic and steric properties on the pyridazine ring results in two different metal-to-ligand ratios.

Electrochemical Properties of the Complexes

Redox properties of complexes **4–6**, **8**, and **9** were investigated by cyclic voltammetry in dry acetonitrile solutions. Cobalt complex **4** (Figure 3) exhibits two reversible redox waves, which are assigned to the consecutive Co^{II} → Co^I ($E_{1/2}$ –0.111 V) and Co^I → Co⁰ ($E_{1/2}$ –1.008 V) redox processes. An additional pseudo-reversible reduction wave appeared at –1.719 V, possibly due to a coordinated ligand redox process. We observed similar reduction waves for the nickel complexes [$E_{1/2}$ –1.260 V (**5**), $E_{1/2}$ –1.387 V (**8**)], as shown in Figure 4. The free ligands were redox inactive in the cathodic potential region. Upon coordination to the metal center, the ligand oxidations [E_{pa} 0.979 V (**3^{tol}**) and

E_{pa} 1.022 V (**3^{tBu}**)] are shifted to more positive potentials [E_{pa} 1.595 V (**4**), E_{pa} 1.314 V (**5**), E_{pa} 1.672 V (**8**), E_{pa} 1.641 V (**6**), E_{pa} 1.877 V (**9**)]; thus, we expect easier ligand reduction in the complexes (Table 5).

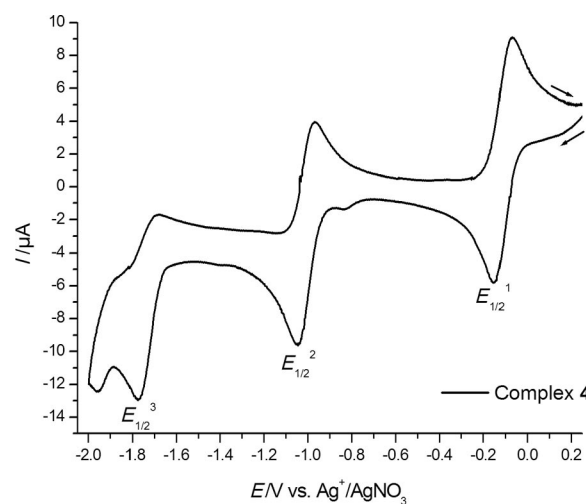


Figure 3. Cyclic voltammogram of complex **4** [Co(**3^{tol}**)₂](NO₃)₂ in acetonitrile solution. Scan rate: 50 mV s^{–1}.

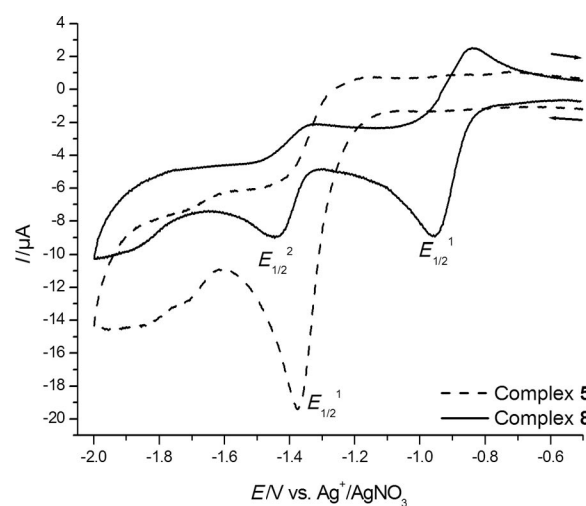


Figure 4. Cyclic voltammograms of complexes **5** [Ni(**3^{tol}**)₂](NO₃)₂ and **8** [Ni(**3^{tBu}**)(NO₃)₂] in acetonitrile solution. Scan rate: 50 mV s^{–1}.

An additional reversible reduction couple M^{II} → M^I was observed for the nickel(II) complex **8** ($E_{1/2}$ –0.901 V), which is more negative than the cobalt(II) complex **4** ($E_{1/2}$ –0.111 V) due to the electronic configuration of Ni^{II} (t_{2g}⁶e_g²). Nickel complex **5** employing ligand **3^{tol}** shows a 2:1 stoichiometry and a N₆ coordination environment around the metal center in the solid state in contrast to metal complex **8**, which shows a N₃O₃ coordination sphere. Thus, the electron density at the metal center is expected to be higher than that in **8**, explaining the lower $E_{1/2}$ value as electrochemical reduction is hindered. This suggests that in solution the same complex stoichiometries are present as in the solid state.

Table 5. Electrochemical data for **4–6**, **8**, and **9** in acetonitrile solution at room temperature.^[a]

Compound	E_{pc} /V	E_{pa} /V	ΔE_p /mV	$E_{1/2}$ /V	Redox process
[Co(^{tol}) ₂](NO ₃) ₂ (4)	−0.153	−0.069	84	−0.111	Co ^{II} → Co ^I
	−1.046	−0.970	76	−1.008	Co ^I → Co
	−1.775	−1.662	113	−1.719	L → L ^[b]
[Ni(^{tol}) ₂](NO ₃) ₂ (5)		1.595			L → L ^[c]
	−1.373	−1.146	227	−1.260	L → L ^[b]
		1.314			L → L ^[c]
[Ni(^{3tBu})(NO ₃) ₂] (8)	−0.955	−0.846	109	−0.901	Ni ^{II} → Ni ^I
	−1.453	−1.321	132	−1.387	L → L ^[b]
		1.672			L → L ^[c]
[Cu(^{tol})(NO ₃) ₂] (6)	−0.820	−0.604	216	−0.712	Cu ^{II} → Cu
		1.641			L → L ^[c]
[Cu(^{3tBu})(NO ₃) ₂] (9)	−0.808	−0.606	202	−0.707	Cu ^{II} → Cu
		1.877			L → L ^[c]
3 ^{tol}		0.979			L → L ⁺
3 ^{tBu}		1.022			L → L ⁺

[a] Measured by CV in CH₃CN at 50 mV s^{−1}. E vs. Ag/AgNO₃. Conditions: Pt disc (working) and Ag/AgNO₃ (reference) electrodes, supporting electrolyte 0.05 M TBAP solution in CH₃CN in an Ar atmosphere. [b] Ligand-centered reduction process upon coordination to the metal, not observed in the CV of the parent ligand in the explored region of 0 to −2.5 V. [c] Ligand-centered oxidation process, facilitated upon coordination to the metal.

Cyclic voltammograms of copper complexes **6** and **9**, as depicted in Figure 5, show both pseudo-reversible redox couples with cathodic reductions at −0.820 V and −0.808 V, respectively, as well as oxidative responses with narrow widths and high peak currents at −0.604 V and −0.606 V, which is typical for anodic stripping of copper metal.^[47]

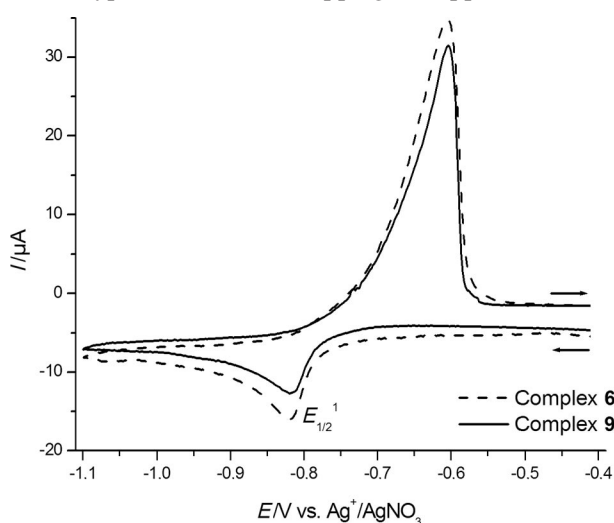


Figure 5. Cyclic voltammograms of complexes **6** [Cu(^{tol})₂](NO₃)₂ and **9** [Cu(^{3tBu})₂](NO₃)₂ in acetonitrile solution. Scan rate: 50 mV s^{−1}.

Conclusions

We have developed a new class of tridentate pyridazine ligands. In contrast to known ligands containing this heterocycle, they feature donor substituents at only one position adjacent to the two nitrogen atoms. This leads to li-

gands reminiscent of the methylated PAPHY ligand, but exhibiting completely different electronic features. We discovered two complex stoichiometries upon coordination to various first-row transition metals depending on the substituents at the 6-position of the heterocycle. We found bis complexes with two ligands coordinated to the metal, which is a prerequisite for the formation of the knots of grids, nets, and cross-linked polymeric networks impressively demonstrated by Lehn and co-workers.^[29–31] Additionally, we found stable mono complexes with only one ligand and two nitrate ions, featuring easily accessible metal centers, which are desirable for versatile catalytic applications. Here-with, we have presented a powerful tool to direct the stoichiometry of the formed complexes by simple variation of the substituents. Furthermore, we proved by cyclic voltammetry that the complexes exhibit in solution the same stoichiometry as in the solid state. The well-behaved character of the compounds makes them suitable building blocks for the design of novel materials.

Experimental Section

General Considerations: The chloropyridazines, 3-chloro-6-(4-methylphenyl)pyridazine (**1**^{tol}) and 3-chloro-6-(*tert*-butyl)pyridazine (**1**^{tBu}), were prepared according to literature procedures.^[32,33] All other chemicals were purchased from commercial sources and used without further purification. All NMR spectra were measured with a Bruker AMX 360 spectrometer (360 MHz for ¹H NMR) or a Bruker Avance III spectrometer (300 MHz for ¹H and 75 MHz for ¹³C NMR). The ¹H NMR spectroscopic data are reported as s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, shifts in ppm relative to the solvent residual peak. All melting points were determined with a Büchi Melting Point B-540 apparatus. Infrared spectra were measured with a Perkin–Elmer FTIR 1725X apparatus by using KBr discs. Room-temperature magnetic susceptibilities, μ_{obs} in BM, and the number of unpaired electrons (u. e.) were determined by the Evans' method^[34] in [D₆]dmsO/3% benzene.

3-(1-Methylhydrazine)-6-(4-methylphenyl)pyridazine (2**^{tol}):** A suspension of 3-chloro-6-(4-methylphenyl)pyridazine (**1**^{tol}) (8.20 g, 40 mmol) in ethanol (100 mL) was heated to reflux. Methylhydrazine (10.7 mL, 200 mmol) was added to the resulting solution. The reaction mixture was heated to reflux for an additional 10 h, after which full conversion was evidenced by TLC analysis. After cooling the solution to room temperature, a white precipitate was formed, which was filtered off and washed with ice-cooled ethanol. Recrystallization from hot ethanol afforded 6.6 g (77%) of pure **2**^{tol}. M.p. 141 °C. ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 2.41 (s, 3 H, CH₃), 3.44 (s, 3 H, NCH₃), 4.11 (br. s, 2 H, NH₂), 7.42 (d, J = 8.1 Hz, 2 H, ArH), 7.43 (d, J = 9.5 Hz, 1 H, ArH), 7.62 (d, J = 9.5 Hz, 1 H, ArH), 7.90 (d, J = 8.1 Hz, 2 H, ArH) ppm. ¹³C NMR (300 MHz, CDCl₃, 298 K): δ = 21.3 (CH₃), 41.1 (N-CH₃), 114.2, 125.0, 125.8, 129.5, 134.1, 138.6, 151.1, 160.8 (aromatic carbons) ppm.

3-(1-Methylhydrazine)-6-(*tert*-butyl)pyridazine (2**^{tBu}):** To a suspension of 3-chloro-6-(*tert*-butyl)pyridazine (3.50 g, 20.5 mmol) in dry ethanol (50 mL) was added methylhydrazine (5.4 mL, 102.6 mmol), and the mixture was heated to reflux for two days. After full conversion (evidenced by TLC analysis) all volatiles were removed under reduced pressure. The yellow residue was dissolved in dichloro-

methane, and the resulting solution was washed with water. The solvent was removed in vacuo to afford 2.8 g (77%) of pure **2^{tBu}** as a light brown oil. ¹H NMR (300 MHz, CDCl₃, 300 K): δ = 1.36 [s, 9 H, C(CH₃)₃], 3.34 (s, 3 H, NCH₃), 4.02 (br. s, 2 H, NH₂), 7.27 (d, *J* = 9.5 Hz, 1 H, ArH), 7.32 (d, *J* = 9.5 Hz, 1 H, ArH) ppm. ¹³C NMR (300 MHz, CDCl₃, 300 K): δ = 30.0 [C(CH₃)₃], 36.0 [C(CH₃)₃], 41.2 (NCH₃), 114.3, 124.6, 160.7, 161.4 (aromatic carbons) ppm.

3^{tol}: An ethanol solution (60 mL) of **2^{tol}** (2.00 g, 9.3 mmol) and 2-pyridine aldehyde (1.1 equiv., 1.10 g, 0.98 mL, 10.3 mmol) in the presence of acetic acid (3 drops) as a catalyst were heated to reflux for 45 min. After cooling to room temperature, the mixture was poured on ice. The cloudy off-white precipitate was filtered off and dried in vacuo. Recrystallization from hot ethanol yielded 2.58 g (96%) of **3^{tol}** as a white crystalline solid. M.p. 187 °C. ¹H NMR (300 MHz, [D₆]dmsO, 300 K): δ = 2.37 (s, 3 H, CH₃), 3.81 (s, 3 H, NCH₃), 7.33 (m, 3 H, ArH), 7.84 (t, *J* = 7.5 Hz, 1 H, ArH), 7.86 (s, 1 H, CH=N), 7.97 (d, *J* = 7.8 Hz, 2 H, ArH), 8.05 (m, 3 H, ArH), 8.60 (br. s, 1 H, ArH) ppm. ¹³C NMR (300 MHz, [D₆]dmsO, 300 K): δ = 20.5 (CH₃), 29.7 (NCH₃), 115.3, 119.2, 122.6, 125.3, 125.6, 129.1, 133.1, 136.3, 136.9, 138.4, 149.0, 152.8, 154.0, 157.7 (aromatic and imino carbons) ppm. IR (KBr): ν̄ = 776 (m), 822 (s), 974 (m), 1102 (m), 1156 (m), 1176 (m), 1426 (s), 1460 (s), 1568 (m), 2355 (w), 2358 (w), 3434 (m, br) cm⁻¹. C₁₈H₁₇N₅ (303.4): calcd. C 71.27, H 5.65, N 23.09; found C 70.61, H 5.32, N 23.00.

3^{Bu}: An ethanol solution (60 mL) of **2^{Bu}** (2.00 g, 11.1 mmol) and 2-pyridine aldehyde (1.0 equiv., 1.19 g, 1.06 mL, 11.1 mmol) in the presence of acetic acid (3 drops) as a catalyst were heated under reflux for 45 min. After cooling the solution, all volatiles were removed under reduced pressure, yielding 2.84 g (95%) of **3^{Bu}** as a light brown oil. ¹H NMR (300 MHz, [D₆]dmsO, 300 K): δ = 1.35 [s, 9 H, C(CH₃)₃], 3.75 (s, 3 H, NCH₃), 7.32 (dd, *J* = 5.5, 6.7 Hz, 1 H, ArH), 7.69 (d, *J* = 9.5 Hz, 1 H, ArH), 7.83 (t, *J* = 7.8 Hz, 1 H, ArH), 7.85 (s, 1 H, N=CH), 7.96 (d, *J* = 9.5 Hz, 1 H, ArH), 8.02 (d, *J* = 7.8 Hz, 1 H, ArH), 8.58 (d, *J* = 4.8 Hz, 1 H, ArH) ppm. ¹³C NMR (300 MHz, [D₆]dmsO, 300 K): δ = 29.7 [C(CH₃)₃ + C(CH₃)₃], 36.0 (NCH₃), 115.3, 119.1, 122.9, 125.4, 136.3, 136.4, 149.1, 154.3, 157.4, 163.5 (aromatic and imino carbons) ppm. IR (KBr): ν̄ = 776 (m), 842 (m), 972 (s), 1136 (s), 1284 (s), 1428 (s), 1464 (s), 1480 (s), 1574 (s), 1714 (m), 2342 (m), 2362 (m), 2960 (s), 3422 (m, br) cm⁻¹. C₁₅H₁₉N₅ (269.3): C 66.89, H 7.11, N 26.00; found C 66.87, H 7.03, N 25.39.

Synthesis of the Complexes

General Procedure: To a boiling solution of the ligand (100 mg) in ethanol (40 mL) was added the metal salt [Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O or Zn(NO₃)₂·4H₂O] (1 equiv., 0.1 M solution in ethanol). A color change was immediately apparent. The reaction mixtures were heated to reflux for additional 20 min followed by cooling to room temperature. The products crystallized after several days. The crystals obtained were isolated by filtration and dried in vacuo. For all compounds single crystals suitable for X-ray diffraction analysis were obtained. The specific crystallization methods are described below.

[Co(3^{tol})₂](NO₃)₂ (4): Following the general procedure by employing **3^{tol}** (0.1 g, 0.35 mmol) and Co(NO₃)₂·6H₂O (0.35 mmol, 3.5 mL of a 0.1 M ethanol solution), compound **4** was obtained as red needles (138 mg, 47% based on the ligand) by crystallization by means of slow evaporation of the solvent at room temperature. IR (KBr): ν̄ = 786 (s), 810 (s), 986 (s), 1032 (s), 1128 (s), 1160 (s), 1304 (s), 1350 (s, br), 1430 (s), 1452 (s), 1544 (s), 1588 (s), 1606 (s), 2398 (w), 2406 (w), 3042 (s, br), 3436 (m, br) cm⁻¹.

CoC₃₀N₁₀H₃₈·H₂O (434.6): calcd. C 53.54, H 4.49, N 20.81; found C 53.31, H 4.29, N 20.61.

[Ni(3^{tol})₂](NO₃)₂ (5): Following the general procedure by employing **3^{tol}** (0.1 g, 0.35 mmol) and Ni(NO₃)₂·6H₂O (0.35 mmol, 3.5 mL of a 0.1 M ethanol solution), compound **5** was obtained as red columns (124 mg, 85% based on the ligand) by crystallization at room temperature for 2 d. IR (KBr): ν̄ = 786 (m), 810 (m), 988 (m), 1034 (m), 1130 (s), 1304 (s), 1338 (s), 1352 (s), 1452 (s), 1546 (m), 1588 (m), 1612 (m), 2350 (w), 2378 (w), 3028 (m), 3052 (m), 3436 (m, br) cm⁻¹. NiC₃₆N₁₂H₃₄O₆·CH₃CH₂OH·0.5H₂O (844.5): C 54.15, H 4.42, N 21.05; found C 54.06, H 4.46, N 20.55.

[Cu(3^{tol})₂](NO₃)₂ (6): Following the general procedure by employing **3^{tol}** (0.1 g, 0.35 mmol) and Cu(NO₃)₂·3H₂O (0.35 mmol, 3.5 mL of a 0.1 M ethanol solution), compound **6** was obtained as green blocks (149 mg, 87%) by crystallization by means of slow evaporation of the solvent at room temperature. IR (KBr): ν̄ = 776 (m), 822 (m), 990 (m), 1014 (m), 1042 (m), 1130 (s), 1238 (m), 1290 (s), 1302 (s), 1384 (s), 1446 (s), 1484 (s), 1554 (m), 1592 (m), 1610 (m) cm⁻¹. CuC₁₈N₇H₁₇O₆·1.5H₂O (517.9): C 41.74, H 3.89, N 18.93; found C 41.43, H 3.36, N 19.02.

[Zn(3^{tol})₂](NO₃)₂ (7): Following the general procedure by employing **3^{tol}** (0.1 g, 0.35 mmol) and Zn(NO₃)₂·4H₂O (0.35 mmol, 3.5 mL of a 0.1 M ethanol solution), compound **7** was obtained as colorless needles (122 mg, 83% based on the ligand) by crystallization at room temperature overnight. ¹H NMR (300 MHz, [D₆]dmsO, 300 K): δ = 1.05 (t, 1.5 H, CH₃, EtOH), 2.38 (s, 3 H, CH₃), 3.34 (dt, 1 H, CH₂, EtOH), 3.84 (s, 3 H, NCH₃), 4.35 (t, 0.5 H, OH, EtOH), 7.34–7.37 (m, 3 H, ArH), 7.96–8.15 (m, 6 H, ArH), 8.58 (br. s, 1 H, ArH) ppm. No ¹³C NMR spectroscopic data are available because of the poor solubility in [D₆]dmsO. IR (KBr): ν̄ = 788 (m), 810 (s), 986 (s), 1030 (s), 1130 (s), 1302 (s), 1302 (s), 1338 (s, br), 1348 (s), 1450 (s), 1548 (s), 1590 (s), 2404 (m, br), 3052 (m, br), 3470 (m, br) cm⁻¹ ppm. ZnC₃₆N₁₂H₃₄O₆·C₂H₅OH (842.2): C 54.32, H 4.80, N 20.01; found C 53.95, H 4.55, N 20.01.

[Ni(3^{Bu})₂](NO₃)₂ (8): Following the general procedure by employing **3^{Bu}** (0.1 g, 0.37 mmol) and Ni(NO₃)₂·6H₂O (0.37 mmol, 3.7 mL of a 0.1 M ethanol solution), compound **8** was obtained as golden tablets (57 mg, 34%) by crystallization by means of diffusion of diisopropyl ether into the solution of the complex in acetonitrile. IR (KBr): ν̄ = 792 (m), 834 (m), 992 (m), 1018 (m), 1090 (m), 1158 (m), 1240 (m), 1268 (s), 1298 (s), 1310 (s), 1356 (m), 1386 (m) *t*Bu, 1446 (s), 1504 (s), 2324 (w), 2346 (w), 2944 (m, br), 3434 (m, br) cm⁻¹. NiC₁₅N₇H₁₉O₆·CH₃CN (493.1): C 41.41, H 4.50, N 22.72; found C 41.55, H 4.27, N 22.47.

[Cu(3^{Bu})₂](NO₃)₂ (9): Following the general procedure by employing **3^{Bu}** (0.1 g, 0.37 mmol) and Cu(NO₃)₂·3H₂O (0.37 mmol, 3.7 mL of a 0.1 M ethanol solution), compound **9** was obtained as green tablets (104 mg, 62%) by crystallization by means of diffusion of diisopropyl ether into the ethanol solution of the complex. IR (KBr): ν̄ = 798 (m), 836 (m), 994 (m), 1010 (m), 1094 (m), 1156 (m), 1242 (m), 1284 (s), 1302 (s), 1358 (m), 1386 (s) *t*Bu, 1486 (s), 1550 (m), 1590 (m), 1590 (m), 1600 (m), 1616 (m), 2332 (w), 2344 (w), 2362 (w), 2970 (m, br), 3434 (s, br) cm⁻¹. CuC₁₅N₇H₁₉O₆·H₂O (474.9): C 37.94, H 4.46, N 20.64; found C 37.52, H 4.13, N 20.48.

[Zn(3^{Bu})₂](NO₃)₂ (10): Following the general procedure by employing **3^{Bu}** (0.1 g, 0.37 mmol) and Zn(NO₃)₂·4H₂O (0.37 mmol, 3.7 mL of a 0.1 M ethanol solution), compound **10** was obtained as colorless plates (64 mg, 38%) by crystallization in acetonitrile. ¹H NMR (300 MHz, [D₆]dmsO, 300 K): δ = 1.34 [s, br 9 H, C(CH₃)₃], 3.78 (s, 3 H, NCH₃), 7.67–8.54 (m, 6 H, ArH) ppm. No ¹³C NMR spectroscopic data are available because of the poor solubility in

[D₆]dms_o. IR (KBr): $\tilde{\nu}$ = 794 (m), 836 (m), 990 (m), 1014 (m), 1086 (m), 1158 (s), 1240 (m), 1284 (s), 1300 (s), 1356 (m), 1386 (m), 1490 (s), 1550 (m), 1598 (m), 1622 (m), 2322 (w), 2332 (w), 2342 (w), 2360 (w), 2966 (m, br), 3458 (s, br) cm⁻¹. ZnC₁₅N₇H₁₉O₆ · 1.5CH₃CN (520.3): C 41.55, H 4.55, N 22.88; found C 41.51, H 4.41, N 22.10.

X-ray Crystallographic Studies: Intensity data sets for compounds **6** and **7** were collected by using a Stoe four circle diffractometer and for compounds **4**, **5**, and **8–10** by using a Bruker Smart Apex 2 diffractometer, both equipped with a graphite monochromator (Mo- K_{α} radiation, λ = 0.71073 Å) and the latter with a CCD detector. All compounds were measured at 100 K, except for **6**, which was measured at 95 K. The structures were solved by direct methods (SHELXS-97)^[35] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).^[35] The asymmetric units of complexes **4**, **5**, **6**, and **7** contain two metal complex molecules and those of **4** and **7** contain additionally one molecule of ethanol, and that of **5** two molecules of ethanol. In complex **4** the C1S–C2S bond length of the ethanol solvent molecule in the crystal was restrained to 1.50(2) Å. For compound **7** one anion and the ethanol solvent molecule are disordered over two sites, which were refined with site occupation factors fixed at 0.5. For the disordered NO₃⁻ anion, the displacement parameters of the N atom were constrained to be the same, and the six N–O distances were restrained to the same value. Appropriate restraints were also applied to the disordered ethanol solvent molecule. All other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. Data were corrected for absorption and Lp factors with SADABS.^[36] Hydrogen atoms were placed geometrically and refined by using a riding model.

CCDC-757211 (for **4**), -757212 (for **5**), -757526 (for **6**), -757527 (for **7**), -757214 (for **8**), -757215 (for **9**), and -757213 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical Methods: Redox chemical properties of complexes **4–6**, **8**, and **9** were carried out in an argon-filled glove box by using a Gamry Reference 600 potentiostat connected to a personal computer. Cyclic voltammograms were obtained in 0.05 M solution [*n*Bu₄N][PF₆]/CH₃CN at 25 °C. The experiments were carried out in a three-electrode glass cell with a platinum disc (d = 3 mm) working electrode, a platinum wire auxiliary electrode, and a {Ag⁺/AgNO₃ 0.01 M in CH₃CN, 0.1 M [*n*Bu₄N][PF₆]} reference electrode. Under these conditions, oxidation of ferrocene occurs at 0.095 V.

Supporting Information (see footnote on the first page of this article): ¹H and ¹³C NMR spectra for **3^{tol}** and **3^{Bu}** in [D₆]dms_o, molecular views of complexes **4**, **6**, **7**, and **10**, and experimental procedure for measurements by Evans' method.

Acknowledgments

Financial support from fFORTE - Wissenschaftlerinnenkolleg FreChe Materie is gratefully acknowledged.

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Received: February 2, 2010
Published Online: April 16, 2010