Ditopic Hexadentate Ligands with a Central Dihydrobenzo-diimidazole Unit Forming a [2x2] Zn₄ Grid Complex

Bernhard Schäfer,[a] Nithin Suryadevara,[a] Jean-Francois Greisch,[a] Olaf Fuhr,[a, b] Manfred M. Kappes,[a, c] and Mario Ruben*[a, d, e]

A family of ditopic hexadentate ligands based on the parent compound 2,6-bis(6-(pyrazol-1-yl)pyridin-2-yl)-1,5-dihydrobenzo[1,2-d:4,5-d']diimidazole (L) was developed and synthesized by using a straightforward condensation reaction, which forms the interlinking central benzo[1,2-d:4,5-d']diimidazole bridge in the ligand backbone. The two secondary amine groups of the benzodiimidazole unit tautomerize and allow the formation of two tauto-conformers, which upon treatment with metal salts forms different isomeric coordination complexes. Here we report six new derivatives (1–6) that can tautomerize (varying the pyrazolopyridine part) and 14 derivatives (7–13) with different alkyl and benzyl substitution on secondary amino groups (of L) that prevent the tautomerization. This way, it is possible to study the properties of isomeric coordination complexes and their intrinsic cooperativity by the example of [2x2] grid complexes in the future. A [2x2] Zn₄ complex of the ligand L was synthesized and structurally characterized.

Introduction

Ditopic ligands are of continuing interest to the covalent integration of metal ions into molecular metal complexes.[1] Such ligands with at least two metal-binding domains can be used to synthesize homo and hetero multi-metallic complexes such as metal-containing supramolecular and macromolecular species (polymers, dendrimers, molecular wires) and oligonuclear grid type metal complexes.[2–5] If the coordination sites of ditopic ligands differ in their metal-chelating properties, discrimination by means of optimized synthetic protocols can yield hetero-metallic complexes.[6,7] The resulting complexes feature different catalytic, magnetic, and photophysical properties and may enable new cooperative functionality.[8–12] In this context, a number of bimetallic complex catalysts have been reported, e.g., in asymmetric allylic alkylation,[13] water oxidation,[14–18] epoxidation,[19] and transfer hydrogenation of ketones.[20] The probably most adaptable and established ligands for this purpose are derivatives of 2,2':6',2"-terpyridine (terpy) type containing, inter alia, pyrazole, tetrazole, and imidazole subunits.[21–29]

Whereas a number of ligands with tridentate chelates and tautomeric subunits have been described previously,[25,30,31,32,33] we are not aware of any examples that describe the presence of different tauto-conformers and the parallel formation of isomeric reaction products upon coordination to transition metal ions.

Recently, we reported on a homoditopic ligand L, which consists of two tridentate 2-(1H-imidazol-2-yl)-6-(pyrazol-1-yl) pyridine units interlinked via a central benzo[1,2-d:4,5-d'] diimidazole bridge (red, Figure 1a).[34] This bridging unit can simultaneously undergo two tautomerization processes between a secondary amine and imine functional groups. Besides, conformational isomers can be formed by rotation about the single bonds between the aromatic ring systems in the backbone of the ligand (Figure 1a). The rotational barriers of the single bonds connecting the pyridine and imidazole subunits enable two in-plane conformations, so-called S and C conformations (this denomination arises from their apparent shape, see Figure 1c). These two conformations are stabilized by the interaction between the N-based lone pair electrons and the H atoms of the neighboring aromatic rings (see Figure 1b).

The investigation of a solution sample of L by ¹H NMR spectroscopy revealed that both tauto-conformers are present in the solution and the L Ş L ratio of one was estimated from ¹H
NMR studies in (deuterated) DMSO. Both tauto-conformers, \( L_S \) and \( L_C \), can coordinate with metal ions in two tridentate binding pockets. The different chelating modes of the homoditopic ligand \( L \) were read out by coordination with \( \text{Fe}^{II} \) ions. This read-out took place in parallel, and multiple coordination products differing in their structures and properties have been observed. Among them, the two dominant, isomeric tauto-conformers \( [\text{Fe}_4(L_S)_4]^8^+ \) and \( [\text{Fe}_4(L_C)_4]^8^+ \) of the \([2\times2]\) \( \text{Fe}^{II}_4 \) grid-type complexes were isolated as crystals by several steps of fractional crystallization.

In the present work, we describe the synthesis, structures, and properties of some members of this new ligand family with respect to the substitution at the periphery and also to the central part of the ligand backbone, so that the ligands could not tautomerize; thus parallel product formation can be avoided. Here, we also present a coordination complex with \( \text{Zn}^{2\+} \) metal ions and describe its properties.

**Results and Discussion**

The tauto-isomerization processes of the ligands and the formed complexes are interesting in themselves and may give insights regarding the general mechanisms of such tauto-isomerization processes. In the following, we will discuss the synthesis of six new ligands with a free \( \text{NH} \) group at the imidazole subunit but differing in their aromatic backbone. The intrinsic electronic and steric properties of ligand \( L \) can be easily adapted, which is apparent from the synthetic procedure shown in Scheme 1. The last step in the ligand synthesis is the condensation reaction of a carboxylic acid derivative (C) and a half equivalent of 1,2,4,5-benzenetetramine tetrahydrochloride in polyphosphoric acid (PPA). The character of the peripheral aromatic rings in the ligand can be determined in the synthetic step (a), where a suitable pyrazole derivative can be chosen (see R: 1–4 in Scheme 1). In the case of a peripheral pyridine substitution, as shown for 5 and 6, we employed the respective \([2,2\′\text{-bipyridine}]\_6\text{-carboxylic acid} \), which was prepared either from \( 2,2\′\text{-bipyridine} \) or \( 6\′\text{-methyl-[2,2\′\text{-bipyridine}]_6\text{-carboxylic acid} \) in two steps. The final condensation reaction between the carboxylic acid derivative and benzene tetraamine in polyphosphoric acid (PPA) forms the respective ligand \( (1–6) \) in good yields.

The synthesized ligands 1 to 6 were entirely characterized by standard methods like \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectroscopy, mass spectrometry, and elemental analysis. It was possible to determine the molecular structure of 3 and 5 by X-ray diffraction of single crystals crystallized from deuterated DMSO with a drop of \( \text{CF}_3\text{COOD} \). Therefore, we found the compounds in the form of their dicaticonic triflate salts, showing a twofold protonation of each imidazole moiety (Figure 2). For comparison, Figure 2 also shows the reported compound L, which was crystallized as a neutral ligand from the DMF solution. All three

![Figure 1](https://example.com/figure1.png)

**Figure 1.** a) The conformational isomerism and tautomerism of \( L \), b) stabilization of the planar ligand configuration by hydrogen contacts in the depicted conformation, c) the \( L_S \) and \( L_C \) conformers of \( L \) as found in solution,\(^{[34]} \) d) the coordination of \( L \) to metal ions (e.g., \( \text{Fe}^{II} \)) develops the tautomerism-driven emergence of complexity (schematic representation of the cationic moieties of the isolated isomers of the \([2\times2]\) \( \text{Fe}^{II}_4 \) grid complexes, consisting of \( L \) (black bars) and \( \text{Fe}^{II} \) ions (grey spheres)).

![Scheme 1](https://example.com/scheme1.png)

**Scheme 1.** Synthesis of the ligands 1 to 6 and the mother compound \( L \) (the first line is only for \( R = \text{pyrazole derivative}; \) in case of \( R \) being a pyridine, refer to Experimental section), a) \( \text{K[pyrazolate], diglyme, 110°C} \) b) \( \text{NaOH, EtOH/H}_2\text{O, 55°C} \) c) \( \text{polyphosphoric acid (PPA), 200°C} \).
structures in Figure 2 show the molecules are in the S configuration (as depicted in Figure 1c).

A detailed examination of the X-ray data shows that the ligand 3 with indazole derivative is not in planar configuration in the crystal lattice. The torsion angles are 18° and 24°, respectively, between the imidazole/pyridine and the pyridine/indazole subunits. The reason for this torsion is the steric stress caused by the interaction between the hydrogen atoms of two opposite aromatic rings, namely the NH hydrogen of the imidazole and the hydrogen in the 7th position of the indazole ring. On the other hand, the ligand 5 has a near planar configuration in the crystal lattice. We calculated a plane out of all C and N atoms of the ligand backbone. Then we measured the distance between each carbon and nitrogen atom of the ligand 5 to this plane, calculating an average distance of 0.05 Å. The ligands are arranged in layers, and the distance between two adjacent layers is 3.36 Å. There are also small torsion angles found for L (1° pyrazole/pyridine and 1° pyridine/imidazole) and 5 (1° pyridine/pyridine and 6° pyridine/imidazole), but these are not caused by steric repulsion between H atoms.

We noticed that the protonation state of the ligand has to be carefully controlled during the workup. Otherwise, hydrochloride or phosphate adducts can form depending on the workup procedure. Since these ligands are hardly soluble in organic solvents that are not miscible with water, it is difficult to adjust the pH as quickly as could be done easily in a biphasic system. We suspended the compounds in aqueous/alcoholic media and changed the pH to the sufficient value (see experimental section for the preparation of 1·2HCl and 1), which is time-consuming since it requires time to work with such an inhomogeneous system. The protonation state of the final product was assessed by elemental analysis. Furthermore, the 1H NMR spectroscopic investigations revealed that the hydrochloride adducts of these ligands 1 to 6 behave slightly different in solution compared to the free ligands.

As mentioned above, both tauto-conformers of L are present in solution, and their ratios could be determined by the integration of the singlet resonances of the central benzene moieties, Hα, Hβ, and Hγ. In the case of DMSO (deuterated), we found an equimolar concentration of L and L, both in dilute and concentrated solutions. This is different for the HCl adducts of such ligands L, 1, 2, 3, and 4, which were precipitated during the workup under acidic conditions. The 1H NMR spectrum of 1·2HCl adducts (with a concentration of 10 to 20 mM dissolved in deuterated DMSO) shows just one single resonance for the central benzene moiety corresponding to Hα. Furthermore, there is no (or only a very broad) signal for the secondary NH group at about 12.5 ppm. Apparently, we just found the S form of the compound from the NMR experiment. A successive dilution of the sample in 3 steps of one order of magnitude each is shown in Figure 3 for 1·2HCl. The relatively sharp Hα resonance (Figure 3a) becomes broader after dilution of one magnitude (Figure 3b) and is almost not visible after the next dilution step (Figure 3c). At a concentration of about 0.015 mM, the signals of Hα, Hβ, and Hγ re-appear as it was observed for the free ligand. This phenomenon was also observed for the hydrochloride adducts of L, 2, 3, and 4 (see ESI, Figures S2-6).

The coordination reaction of the presented ligands with transition metal ions such as Fe2+, Co2+, Zn2+ is generally carried out in solvents like acetonitrile, nitromethane, or methanol. The solubility of the ligands in these solvents is very low. Therefore, we can conclude from the 1H NMR spectroscopic investigation that even for the HCl adducts, both tauto-conformers are present in solution and a divergent coordination34 reaction takes place with at least two main coordination products. The tautomerization of the ligand is interesting and gives access to different coordination modes and products. It is possible to investigate the factors that...
influence the isomerization of the formed grid complexes, such as temperature, solvent polarity, or pH.

However, if we want to study, in detail, the influence of the different coordination modes on the properties of the coordination products in the future, it may be advantageous to block the occurring tautomerization equilibrium of the two different tauto-conformers of L by chemical substitution at the secondary amine functionalities forming tertiary amines. The resulting ligands are either in a C- or S-type conformation which are unable to tautomerize and can be separated easily by column chromatography; thus, any parallel product formation is avoided during divergent coordination protocols. So to block the interconversion in ligand L, we treated it with alkyl or benzyl bromides or iodides either in DMF or DMSO as a solvent in the presence of Cs$_2$CO$_3$ as a base, as depicted in Scheme 2.

The seven pairs of prepared derivatives differ in the steric demand of the introduced substituents. Increasing the chain length of the alkyl substituent may influence the crystal packing of the resulting [2x2] Fe$^4$ grid complexes in the solid-state and, therefore, also plays a role in the Spin Crossover (SCO) property of these compounds as seen before in mononuclear compounds.\[37,38\] The synthesized ligands 7e/7s to 13e/13s were characterized entirely by standard methods like $^1$H and $^{13}$C NMR spectroscopy, mass spectrometry, and elemental analysis (see Experimental Section and ESI). It was possible to determine the molecular structure of 8e, 12c, and 12s by X-ray diffraction of single crystals (see Figure 4 and Table S2). The substitution of the secondary amine group of imidazole ring with alkyl and tert-butylbenzene moieties has improved the solubility of the ligands in solvents like chloroform/methanol, and even in diethyl ether in case of 12.

The diverse nature of the prepared derivatives of L will allow in future a detailed study of different metal complexes prepared from these structurally related ligands and may uncover resulting structure-property relationships. As one first example, we want to report on a Zn$_4$ grid complex prepared from the reaction of equimolar amounts of L with the metal salt Zn(ClO$_4$)$_2$·6H$_2$O in acetonitrile. The complex formation leads to a clear yellow solution of a metal complex [Zn$_4$(L)$_4$](ClO$_4$)$_8$. The $^1$H-NMR spectroscopic investigation of a sample of the reaction mixture showed 84% of the [Zn$_4$(L)$_4$]$_{18+}$ and 16% of a second complex, [Zn$_4$(L)$_4$](ClO$_4$)$_8$ isomer, comparing the NMR data with the data of the Fe$^4$ grid derivatives described elsewhere.\[34\] The second data set of the [Zn$_4$(L)$_4$](ClO$_4$)$_8$ isomer disappeared after recrystallization. The major fraction of the reaction product was isolated by slow diffusion of diisopropyl ether into the concentrated acetonitrile solution of the complex. The molecular structure of [Zn$_4$(L)$_4$](ClO$_4$)$_8$ could be determined by X-ray diffraction of single crystals obtained during this recrystallization process (Figure 5b).

So far, it was not possible to isolate the pure [Zn$_4$(L)$_4$](ClO$_4$)$_8$ isomer since both complexes (C and S) are of same color whereas in case of the Fe$^4$ grid complexes, they show differences in their spin states. Figure 6 shows the $^1$H NMR spectrum of the ligand L for comparison, where the C and the S conformation are in equilibrium, giving, therefore, three signals for the singlet resonances of the central benzene moieties, H$_u$, H$_v$, and H$_s$ (see Figure 1c and Figure 6) and the spectrum of [Zn$_4$(L)$_4$](ClO$_4$)$_8$ showing only one resonance H$_u$ for this moiety. Besides NMR spectroscopy in solution and X-ray diffraction of single crystals, we also investigated the properties of [Zn$_4$(L)$_4$](ClO$_4$)$_8$ in the gas phase by high-resolution ESI-TOF mass spectrometry as shown in Figure 7. The mass spectrum of the reaction mixture following the coordination reaction is shown in the supporting information but has not such a high resolution as the one shown in Figure 7.

**Scheme 2.** Synthesis of the ligand pairs of 7 to 13 starting from the mother compound L (using either DMSO or DMF as a solvent and Cs$_2$CO$_3$ as a base for the reaction with the respective haloalkane or benzyl halide, see also the Experimental Section) different tautomers are chemically stabilized in this way so that an interconversion is not possible anymore.

**Figure 4.** X-ray structures of a) 12b, b) 12c, and c) 8c (C black, N green, hydrogen atoms were omitted for clarity).
The absorption spectrum of $[\text{Zn}^4(\text{LS})_4]^{8+}$ in acetonitrile is depicted in Figure 8, the absorption maxima ($\lambda_{\text{max}}$), and extinction coefficients ($\varepsilon$) for the complex are listed in the supporting information. The UV region of the absorption spectrum shows strong bands with maxima at 258 nm, 377 nm, and 394 nm, which corresponds to ligand-centered ($\pi$-$\pi^*$ transition bands. In the free ligand $\text{L}$, these bands are slightly higher in energy (see SI-Figure S33).

**Conclusion**

A family of ditopic hexadentate ligands with a central dihydrobenzo-diimidazole unit based on the mother compound 2,6-bis(6-(pyrazol-1-yl)pyridin-2-yl)-1,5-dihydrobenzo[1,2-d:4,5-d']imidazole ($\text{L}$) were successfully synthesized by condensation reactions. The two tautomerizing secondary amine functionalities of the benzimidazole unit are the origin of two tautomer-conformers, which can translate into two different isomeric coordination complexes. We reported on six tautomerizing derivatives with different nitrogen containing aromatic subunits with different electronic and steric properties. The resulting [2x2] grid complexes of transition metals, e.g., Fe$^{II}$, Co$^{II}$, and the prepared ligands are interesting in themselves, regarding the structure-property relationship of the isomeric complexes and their isomerization equilibrium. The 14 derivatives with different alkyl and benzyl substitution on secondary amino groups do not tautomerize and can give access to only one [2x2] grid...
complex tauto-isomer. In this way, it will be possible to study the properties of isomeric coordination complexes and their intrinsic cooperativity on the models of [2x2] grid complexes in the future. Furthermore, we note that grid complexes built from the 5 form of such ligands show two chiral enantiomers. In the future, we will focus on the deconvolution/separation of these enantiomers and hope to study their properties in detail.

Experimental Section

**General Methods:** All the reactions were performed under Argon atmosphere using standard Schlenk techniques unless specified. All starting materials were purchased from commercial sources and were used as received. Solvents were freshly distilled over appropriate drying reagents. $^1$H and $^{13}$C NMR, COSY, HMQC correlation measurements were recorded using a Bruker Ultrashield plus 500 spectrometer with solvent-proton as an internal standard. Elemental analyses were carried out on a Vario Micro Cube. Infrared spectra were recorded using KBr-pressed pellets with a Perkin-Elmer Spectrum GX FT-IR spectrometer in the region of 4000–400 cm$^{-1}$. Mass spectrometric data were acquired with a MicroTOF-Q II Bruker for ESI-TOF. Electronic absorption and fluorescence spectra were acquired at room temperature for diluted solutions (e.g., $2 \times 10^{-4}$ M) on a Cary 500 Scan UV-VIS-NIR spectrophotometer and a Cary Eclipse fluorospectrophotometer, respectively using a 1 cm quartz cell. For Zinc complex, Mass-spectrometric measurements we performed on a SYNAPT G2S-HDMS (Waters, Manchester, UK) using electrospray ionization.

**X-Ray Crystallographic Data:** Single crystal X-ray diffraction data were collected on a STOE IPSD II or IPDS2T diffractometer with monochromated Mo Kα radiation (0.71073 Å) at low temperatures. Using Olex2,[39] the structure was solved with the ShelXS[40] structure solution program using Direct Methods and refined with the ShelXL[41] refinement package using Least Squares minimization. Refinement was performed with anisotropic temperature factors for all non-hydrogen atoms (disordered atoms were refined isotopically); hydrogen atoms were calculated on idealized positions. Crystal data and structure refinement parameters are summarized in Tables S1–S3 in ESI.

Deposition Numbers 1436806 (for L), 1576574 (for 3), 1576575 (for 5), 1576576 (for 8c), 1576577 (for 12c), 1576578 (for 12s), and 1576579 (for [Zn(L)$_4$][ClO$_4$]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformatonszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

**Synthesis of Ligands and Complex**

**Ligand L:** (6-(pyrazol-1-yl)picolinic acid, 4.13 g, 21.8 mmol, 2.1 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (3.00 g, 10.6 mmol, 1 eq), and polyphosphoric acid (16 mL) were gently heated at 120°C for 3 h and then at vacuo ($T = 90$ °C). **Yield:** 4.27 g, 73%. $^1$H NMR (500 MHz, (CD)$_3$SO, c = 1.3 mM): $\delta = 13.22$ (s, very broad, NH), 9.30 (d, $J = 2.3$ Hz, 2H, H5), 8.28 (d, $J = 7.1$ Hz, 2H, H7), 8.22 (dd (visual triplet), $J_1 = 7.8$ Hz, $J_2 = 7.8$ Hz, 2H, H8), 8.05 (d, $J = 8.0$ Hz, 2H, H9), 7.94 (s, very broad, 2H, Hx), 7.93 (d, $J = 0.9$ Hz, 2H, H3), 6.57 (dd, $J_1 = 2.4$ Hz, $J_2 = 1.7$ Hz, 2H, H4) ppm. **Elemental analysis (EA)** (L$^1$H$_5$O$^1$SO$^1$ClO$_4$ with 0.5(C$_6$H$_5$N$_5$O$_4$Cl)$_{0.5}$ (542.2)):

| C | 54.27 | H | 4.18 | N | 25.83 |
|---|---|---|---|---|---|
| calc. | 54.29, 54.58, 4.45, 25.45 | found | 54.27, 4.18, 25.83 |

**Ligand 1-2HCl:** (6-(3,5-dimethyl-pyrazol-1-yl)picolinic acid), 3.00 g, 13.8 mmol, 2 eq), 1,2,4,5-benzenetetramine tetrahydrochloride (1.82 g, 6.42 mmol, 0.93 eq) and polyphosphoric acid (16 mL) were gently heated at 120°C until the polyphosphoric acid got viscous enough to allow the stirring with a magnetic stirrer bar. Then the temperature was changed gradually to 200°C (Caution: gas evolution leads to foam-formation. After 4 h at 200°C, the reaction was stopped, allowed to cool below 100°C and poured into crushed ice (100 g). The flask was rinsed with water. The aqueous suspensions were combined. The precipitate was filtered off. The solid was suspended in water, and the pH value was altered to 10 using NaOH (3 M). After the suspension was stirred for 1 h, the precipitate was collected again. Afterwards, it was suspended again in water, stirred, the pH was set to about 4 using HCl (1 mol/L). The precipitate was washed with MeOH (125 mL). Finally, the precipitate was suspended in MeOH (100 mL), stirred overnight, collected by filtration, dried in an oven at 120°C for 3 h and then at vacuo ($T = 90$ °C). **Yield:** 4.27 g, 73%. **IR** (KBr): $\nu = 3439, 3099.12, 1641, 1600, 1575, 1521, 1394, 1339, 1291, 1251, 1239, 1203, 1170, 1150, 1137, 1040, 992, 973, 937, 915, 882, 811, 762, 739, 711, 651, 624, 593, 521, 418 cm$^{-1}$. **Mass spectrum of [Zn(L)$_4$][ClO$_4$]**: m/z 467.18 (100 %, [M$^+$+Na$^-$]), IR (KBr): $\nu = 3439, 3099.12, 1641, 1600, 1575, 1521, 1472, 1394, 1339, 1291, 1251, 1239, 1203, 1170, 1150, 1137, 1040, 992, 973, 937, 915, 882, 811, 762, 739, 711, 651, 624, 593, 521, 418 cm$^{-1}$.
evolution leads to foam formation). After 4 hours at 200°C, the reaction was stopped, allowed to cool below 100°C and poured into crushed ice/water mixture (250 mL). The flask was rinsed with water. The aqueous suspensions were combined. The light precipitate was slowly filtered off. The solid chunks were suspended in water by sonication and using a spatula while the pH value was altered to 9 using NaOH (1 M). After the suspension was stirred for 1.5 h the precipitate was collected again. Afterward, it was resuspended in water, stirred, the pH was set to about 3 using HCl (1 mol/L). The compound was suspended in MeOH (V = 100 mL), stirred for 2 h, and collected by filtration. Then the precipitate was suspended in DMSO (250 mL), stirred for 0.5 h, and collected by filtration. Yield: 3.14 g, 83 %. 1H NMR (500 MHz, (CD3)2SO): δ = 12.65 (s, 1H, NH), 12.40 (s, 2H, MeOH), 12.26 (s, 2H, MeOH), 7.83 (s, 1H, 7H, 2H), 7.60 (s, 1H, 7H, 2H), 7.27 (s, 1H, 6H, 3H), 2.25 (s, 6H, 2H), ppm. EA [1H-H2O] (C6H14N2O2): calc C 56.80, H 4.77, N 23.68; found C 56.94, H 5.01, N 23.69, ES-MS (in DMSO): m/z = 253.198 (100%, [M + Na] = ([C6H14N2O2Na]+)).

Ligand 1: Ligand 1-2HCl (2.88 g) was pelleted and suspended in H2O (30 mL) and MeOH (10 mL). The suspension was stirred and the pH was adjusted to 7 by using aqueous NaOH (1 mol/L). The pH value was controlled again after stirring overnight. Finally, the volume was reduced to about 5 mL by rotary evaporation; the precipitate was collected by filtration, dried in an oven (at 120°C) over the weekend. Yield: 2.37 g, 71 %. 1H NMR (500 MHz, (CD3)2SO): δ = 12.46 (s, 2H, NH), 12.45 (s, 2H, NH), 8.28 (d, J = 7.5 Hz, 2H, H4), 8.14 (dd, J = 7.8 Hz, 7.8 Hz, 4H, H5), 8.03 (s, 1H, H1), 7.85 (s, 4H, H6), 7.78 (s, 1H, H2), 6.71 (s, 4H, 2H, CH3), 2.25 (s, 12H, CH2, H2) ppm. EA [1H-H2O] (C12H22N2O2SO3): calc C 64.85, H 5.05, N 27.01; found C 64.57, H 4.64, N 26.78. ES-MS (in DMSO): m/z = 501.218 (100%, [M + H] = ([C12H22N2O2SO3]+)). m/z = 523.200 (100%, [M + Na] = ([C12H22N2O2Na]+)).

Ligand 2-HCl: (6-(3,5-diphenyl-pyrazol-1-yl)pyridin-2-ylidene acetic acid (0.703 g, 3.50 mmol, 2 eq), 1,2,4,5-benzentetramine tetrahydrochloride (0.284 g, 1.00 mmol, 0.9 eq) and polyphosphoric acid (0.116 g, 0.447 mmol, 0.9 eq) were used with procedure and workup same as that of synthesis of 1H NMR (500 MHz, (CD3)2SO): δ = 13.73 (s, 2H, NH), 12.99 (s, 2H, NH), 8.49 (d, J = 7.8 Hz, 2H, py-H4), 8.11 (d, J = 7.8 Hz, 7.8 Hz, 4H, py-H5), 8.01 (d, J = 7.2 Hz, 4H, Ph), 7.75 (s, 2H, broad, Hc), 7.68 (d, J = 7.2 Hz, py-H6), 7.51 (dd, J = 7.6, J = 7.6 Hz, 4H, Ph), 7.41 (m, 1H, Ph), 7.31 (s, 2H, pz) ppm. ES-MS (in DMSO): m/z = 517.18 (100 %, [M + H]+ = ([C12H22N2O2SO3]+)). m/z = 545.17 (20 %, [M + Na] = ([C12H22N2O2Na]+)).

Ligand 2-2HCl: 6-(3,5-diphenyl-pyrazol-1-yl)pyridin-2-ylidene acetic acid (1.00 g, 4.67 mmol, 2.15 eq), 1,2,4,5-benzentetramine tetrahydrochloride (0.616 g, 2.17 mmol, 1 eq) and polyphosphoric acid (16 mL) were used with procedure and workup same as that of synthesis of 1H NMR (500 MHz, (CD3)2SO): δ = 12.97 (s, 2H, NH), 12.91 (s, 2H, NH), 8.81 (dd, J = 13.4, 7.8 Hz, 4H, H4), 8.53 (dd, J = 7.7, 2.3 Hz, 4H, H9), 8.39 (d, J = 7.7 Hz, 4H, H11), 8.18 (t, J = 7.8 Hz, 4H, H10), 8.05 (s, 1H, H7), 7.98 (dd, J = 7.7, 7.7 Hz, 4H, H4), 7.89 (s, 2H, Hx), 7.80 (s, 1H, H7), 7.42 (d, J = 7.6 Hz, 4H, H5), 7.35 (s, 6H, H7) ppm. ES-MS (in DMSO): m/z = 517.18 (100 %, [M + Na] = ([C12H22N2O2Na]+)). m/z = 545.17 (20 %, [M + Na] = ([C12H22N2O2Na]+)). m/z = 573.26 (40 %, [2 M + Na] = ([2C12H22N2O2Na]+)).

Ligand 3: 6-[(4-(4-(tert-butyl)phenyl)-pyrazol-1-yl)pyridin-2-ylidene acetic acid (2.90 g, 9.02 mmol, 2 eq), 1,2,4,5-benzentetramine tetrahydrochloride (1.19 g, 4.19 mmol, 0.93 eq) and polyphosphoric acid (20 mL) were used with procedure and workup same as that of synthesis of 1H NMR (500 MHz, (CD3)2SO): δ = 13.00 (s, 2H, NH), 12.85 (s, 2H, NH), 8.39 (d, J = 7.7 Hz, 4H, H4), 8.12 (t, J = 7.7 Hz, 7.8 Hz, 4H, H9), 8.11 (t, J = 7.6 Hz, 4H, H11), 8.05 (d, J = 7.7 Hz, 4H, H5), 7.97 (s, 2H, broad, Hc), 7.95 (d, J = 7.4 Hz, 4H, H6), 7.53 (t, J = 7.6 Hz, 4H, H7), 7.36 (t, J = 7.3 Hz, 2H, H8) ppm. ES-MS (in DMSO): m/z = 517.18 (100 %, [M + H]+ = ([C12H22N2O2]+)). m/z = 545.17 (20 %, [M + Na] = ([C12H22N2O2Na]+)).
**Chemistry Europe**

**Journal of the Chemical Society, Perkin Transactions 2**

**Title:** Synthesis, Spectroscopic Characterization, and Reactivity of New Metal Complexes with Chelating Tetraaza- and Triaza-substituted Ligands

**Authors:**
- [First Name] [Last Name]
- [First Name] [Last Name]

**Abstract:**

This paper presents the synthesis, spectroscopic characterization, and reactivity of new metal complexes with chelating tetraaza- and triaza-substituted ligands. The complexes were synthesized using a variety of metal ions, and their structures were determined using a combination of 1H NMR, IR, and mass spectrometry. The reactivity of these complexes was studied using a series of reactions, and the results indicate promising potential for application in various fields such as catalysis and medicinal chemistry.

**Keywords:** Tetraaza, Triaza, Metal Complexes, Spectroscopy, Reactivity

**Introduction:**

Chelating ligands with nitrogen donor atoms have been the subject of extensive research due to their versatile coordination chemistry and potential applications in various fields. In this study, we report the synthesis and characterization of new metal complexes with tetraaza- and triaza-substituted ligands. The ligands were designed to coordinate with metal ions in a chelating fashion, leading to the formation of stable complexes.

**Results and Discussion:**

The ligands were synthesized by condensing appropriate amines with 1,2-diaminoethane under basic conditions. The metal complexes were formed by reacting the ligands with metal salts in methanol or ethanol solutions. The structures of the complexes were confirmed by 1H NMR, IR, and mass spectrometry. The IR spectra showed characteristic absorptions for the ligand functionalities, and the mass spectra confirmed the molecular weights and charge states of the complexes.

Some of the complexes showed interesting reactivity patterns. For example, the tetraaza complex with Cu(II) showed a significant shift in the ligand's absorption bands, indicating a change in the electronic structure of the ligand. The reactivity of the complexes with various reagents was also investigated, and the results suggest potential applications in catalytic processes.

**Conclusion:**

The synthesis and characterization of new metal complexes with chelating tetraaza- and triaza-substituted ligands have been successfully achieved. The complexes show promising reactivity patterns that warrant further investigation for potential applications in catalysis and medicinal chemistry.

**Acknowledgment:**

The authors would like to thank [Institution] for financial support and [Professor Name] for helpful discussions.

**References:**

1. [Reference 1 Title]
2. [Reference 2 Title]

**Supporting Information:**

- Spectroscopic data for all complexes
- Synthetic procedures for ligand and complex preparation

**Corresponding Author:**
- [Name]
- [Institution]
- [Email]

**ORCID:**
- [Unique ID]

**Conflict of Interest:**

The authors declare no conflict of interest.

**Open Access:**

This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

**Disclosure:**

This is an open-access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

**Data Availability:**

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Ethics Approval:**

This study does not involve any human or animal subjects.

**Consent to Participate:**

All participants provided written informed consent.

**Consent for Publication:**

All authors have read and agreed to the submitted version of the manuscript.

**Funding:**

This research was funded by [Funding Agency Name] through grant number [Grant Number].

---

**Table 1: Properties of Metal Complexes**

| Complex   | Metal   | Coordination Number | Stability | Reactivity | XPS Data |
|-----------|---------|---------------------|-----------|------------|----------|
| [Cu(L)₂]  | Cu(II)  | 4                   | Stable    | Activated  | Cu:39.5% |
| [Ni(L)₂]  | Ni(II)  | 4                   | Stable    | Inactive   | Ni:27.8% |
| [Zn(L)₂]  | Zn(II)  | 4                   | Stable    | Activated  | Zn:19.2% |

---

**Figure 1: XPS Spectra**

The XPS spectra of the complexes show characteristic peaks for the metal and ligand elements, indicating the successful formation of the complexes.

---

**Figure 2: NMR Spectra**

The 1H NMR spectra of the complexes display characteristic signals for the ligand protons, confirming the coordination modes.

---

**Figure 3: Mass Spectra**

The mass spectra of the complexes show molecular ions, indicating the molecular weights and charge states.

---

**Figure 4: Reactivity Profiles**

The reactivity profiles of the complexes show changes in the reaction rates and product yields, indicating their potential applications in catalysis.

---

**Figure 5: Thermogravimetric Analysis**

The thermogravimetric analysis of the complexes shows weight loss in the range of 50-200°C, indicating their thermal stability.

---

**Figure 6: Optical Properties**

The optical spectra of the complexes show absorptions in the UV-visible region, indicating their potential applications in photonic materials.

---

**Figure 7: Electrochemical Properties**

The electrochemical properties of the complexes show redox peaks, indicating their potential uses in redox chemistry.

---

**Figure 8: Catalytic Activity**

The catalytic activity of the complexes was tested in various reactions, showing promising results in terms of turnover numbers and selectivities.

---

**Figure 9: Spectroscopic Characterization**

The spectroscopic characterization of the complexes was performed using various techniques, confirming their structures and providing insights into their coordination modes and electronic properties.

---

**Figure 10: Computational Studies**

The computational studies of the complexes were carried out using density functional theory, providing insights into their electronic structures and coordination geometries.

---

**Figure 11: Biological Activity**

The biological activity of the complexes was tested against various microbial strains, showing promising antibacterial and antifungal properties.

---

**Figure 12: Materials Synthesis**

The synthesis of the complexes involved a series of reactions, providing insights into their synthetic routes and potential applications.

---

**Figure 13: Structural Analysis**

The structural analysis of the complexes was performed using X-ray crystallography, providing detailed information about their crystal structures and packing motifs.

---

**Figure 14: Catalytic Mechanism**

The catalytic mechanism of the complexes was proposed based on the experimental data, providing insights into their reaction pathways and intermediates.

---

**Figure 15: Product Distribution**

The product distribution of the complexes was studied in various reactions, showing a broad range of products with high yields.

---

**Figure 16: Kinetic Studies**

The kinetic studies of the complexes were performed using stopped-flow techniques, providing insights into their reaction rates and activation parameters.

---

**Figure 17: Drug Delivery**

The drug delivery properties of the complexes were evaluated using in vitro and in vivo assays, showing promising results in terms of bioavailability and drug release.

---

**Figure 18: Toxicity Assessment**

The toxicity assessment of the complexes was carried out using various in vitro and in vivo models, showing low toxicity and promising biocompatibility.

---

**Figure 19: Environmental Impact**

The environmental impact of the complexes was evaluated using life-cycle assessment, showing low environmental footprints.

---

**Figure 20: Sustainability Practices**

The sustainability practices in the synthesis and characterization of the complexes were highlighted, including the use of environmentally friendly solvents and reagents.

---

**Figure 21: Future Directions**

The future directions in the research of the complexes were outlined, highlighting potential applications in various fields and the need for further studies.

---

**Figure 22: Conclusion**

The study provides new insights into the synthesis, characterization, and reactivity of metal complexes with chelating tetraaza- and triaza-substituted ligands, opening up new avenues for their applications in various fields.
Ligand 10: The reaction was carried out as described for compound 8 using: L (0.895 g, 2.02 mmol, 1 eq), Cs₂CO₃ (2.65 g, 8.10 mmol, 4 eq), DMСO (20 mL) and 1-ido-hexane (0.856 g, 4.04 mmol, 2 eq, V = 0.528 mL). Yield: 10C: 0.186 %, 16%, 10C: 0.469 %, 38 %.

Ligand 105: 'H NMR (500 MHz, CDCl₃): δ = -8.54 (d, J = 7.5 Hz, 2H, H5), 8.38 (d, J = 7.5 Hz, 2H, H7), 8.10 (d, J = 8.1 Hz, 2H, H9), 8.02 (dd, J = 7.9, J = 7.9 Hz, 2H, H8), 7.86 (2H, H14), 7.81 (d, J = 1.4 Hz, 2H, H3), 6.54 (t, J = 2.4 Hz, J = 1.8 Hz, 2H, H4), 4.92 (t, J = 7.7 Hz, 2H, H14), 2.06 (4H, H15), 1.45 (4H, H16), 1.31 (5H, H8, H17, H18). 0.85 (t, J = 7.1 Hz, 6H, H19) ppm. 13C NMR (126 MHz, CDCl₃/CD₂OD, 5:1): δ = 150.71, 150.43, 143.47, 142.17, 140.05 (CD8), 137.79, 129.98 (C5), 129.92, 125.56 (C29), 121.56 (C27), 112.97 (H9), 108.25 (C4, 98.88 (C5), 45.75 (C14), 31.48 (C17), 29.56 (C16), 22.44 (C18), 13.73 (H19) ppm. EA105 with [Cs₅H₉N₅O₆] 612.8 g/mol: calc. C 70.56, H 6.58, N 22.86, found C 70.40, H 6.68, N 22.85.

H NMR (500 MHz, CDCl₃): δ = 7.95 (d, J = 8.4 Hz, 2H, H2), 7.43 (d, J = 7.9 Hz, 2H, H7), 8.03 (dd, J = 7.9 Hz, 2H, H8). 3.73 (s, 1H, H14), 6.47 (t, J = 2.5 Hz, J = 1.7 Hz, 2H, H4), 4.89 (t, J = 7.9 Hz, 2H, H14), 2.07 (4H, H15), 1.66 (5H, H8, H17, H18). 0.88 (t, J = 7.1 Hz, 6H, H19) ppm. 13C NMR (126 MHz, CDCl₃): δ = 150.72, 149.11, 148.97, 143.30 (H3), 140.40, 139.71 (C3), 136.25, 126.69 (C5), 122.56 (C29), 112.97 (H9), 108.25 (C4, 98.88 (C5), 45.75 (C14), 31.48 (C17), 29.56 (C16), 22.44 (C18), 13.73 ppm. EA105 with [Cs₅H₉N₅O₆] 612.8 g/mol: calc. C 70.56, H 6.58, N 22.86, found C 70.40, H 6.68, N 22.85.

H NMR (500 MHz, CDCl₃): δ = 7.94 (d, J = 8.2 Hz, 2H, H7), 8.00 (d, J = 8.0 Hz, 2H, H8), 8.03 (dd, J = 7.9 Hz, 2H, H8). 3.73 (s, 1H, H14), 6.57 (t, J = 2.5 Hz, J = 1.7 Hz, 2H, H4), 4.95 (t, J = 7.9 Hz, 2H, H14), 2.07 (4H, H15), 1.67 (5H, H8, H17, H18). 0.88 (t, J = 7.1 Hz, 6H, H19) ppm. 13C NMR (126 MHz, CDCl₃): δ = 150.72, 149.11, 148.97, 143.30 (H3), 140.40, 139.71 (C3), 136.25, 126.69 (C5), 122.56 (C29), 112.97 (H9), 108.25 (C4, 98.88 (C5), 45.75 (C14), 31.48 (C17), 29.56 (C16), 22.44 (C18), 13.73 ppm. EA105 with [Cs₅H₉N₅O₆] 612.8 g/mol: calc. C 70.56, H 6.58, N 22.86, found C 70.40, H 6.68, N 22.85.

Full Papers
Acknowledgements

We acknowledge the support by the Deutsche Forschungsgemeinschaft (DFG) SFB/TRR 88 MET (A8 and C6). We also acknowledge the support of the Karlsruhe Nano Micro Facility (KNMF, www.knmf.kit.edu), a Helmholtz Research Infrastructure at Karlsruhe Institute of Technology (KIT, www.kit.edu). Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Divergent · Grid complex · Polypyrrole · Tautomerism · Zinc

[1] E. C. Constable, Coord. Chem. Rev. 2008, 252, 842–855.
[2] U. S. Schubert, H. Hofmeier, G. R. Newkome, Modern Tertiary Chemistry 2006.
[3] H. Hofmeier, U. S. Schubert, Chem. Soc. Rev. 2004, 33, 373–399.
[4] A. Wild, A. Winter, F. Schlüter, U. S. Schubert, Chem. Soc. Rev. 2011, 40, 1459–1511.
[5] E. C. Constable, Chem. Soc. Rev. 2007, 36, 246–253.
[6] C. A. Tovee, C. A. Kilner, S. A. Barrett, J. A. Thomas, M. A. Halcrow, Eur. J. Inorg. Chem. 2010, 1007–1012.
[7] B. Schäfer, T. Bauer, I. Faus, J. A. Wolny, F. Dahms, O. Fuhr, S. Ledebkin, H. C. Wille, K. Schlage, K. Chevalier, F. Rupp, R. Diller, V. Schuenemann, M. M. Kappes, M. Ruben, Dalton Trans. 2017, 46, 2289–2302.
[8] P. Buchwalter, J. Rosé, P. Braunstein, Chem. Rev. 2015, 115, 28–126.
[9] T. K. Roson, T. Lazarides, H. Adams, S. J. A. Pope, D. Sykes, S. Faulkner, S. J. Coles, M. B. Hursthouse, W. Clegg, R. W. Harrington, M. D. Ward, Chem. A Eur. J. 2006, 12, 9299–9313.
[10] H. Ozawa, K. Sakai, Chem. Commun. 2011, 47, 2227–2242.
[11] M. G. Pfeffer, B. Schäfer, G. Smolentsev, J. Uhlig, E. Nazarenko, J. Guthmuller, C. Kuhnht, M. Wächterl, B. Dietzke, V. Sundström, S. Rau, Angew. Chem. Int. Ed. 2015, 54, 5044–5048; Angew. Chem. 2015, 127, S132–S136.
[12] M. D. Ward, Coord. Chem. Rev. 2007, 251, 1663–1677.
[13] A. Ficks, C. Sibbald, M. John, S. Deichert, F. Meyer, Organometallics 2010, 29, 1117–1126.
[14] B. Das, B. L. Lee, E. A. Karlsson, T. Åkermark, A. Skatskis, S. Demeshko, R. Z. Liao, T. M. Laine, M. Haukkia, E. Zeglio, A. F. Abdel-Wagied, P. E. M. Siegbahn, F. Meyer, M. D. Kärkäis, E. V. Johnston, E. Nordlander, B. Åkermark, Dalton Trans. 2016, 45, 13289–13293.
[15] Y. Jiang, F. Li, B. Zhang, X. Li, X. Wang, F. Huang, L. Sun, Angew. Chem. 2013, 125, 3482–3485; Angew. Chem. Int. Ed. 2013, 52, 3398–3401.
[16] H. Y. Wang, E. Mijangos, S. Ott, A. Thapper, Angew. Chem. Int. Ed. 2014, 53, 14499–14502; Angew. Chem. 2014, 126, 14727–14730.
[17] S. Neudeck, S. Maji, I. López, S. Deichert, J. Benet-Buchholz, A. Llobet, F. Meyer, Inorg. Chem. 2016, 55, 2508–2521.
[18] S. Neudeck, S. Maji, I. López, S. Meyer, F. Meyer, L. Aebt, J. Am. Chem. Soc. 2014, 136, 24–27.
[19] J. Aguilló, L. Francς, R. Boffi, M. Gil-SEPULCRE, J. Garcia-Anton, A. Poater, A. Llobet, L. Escriche, F. Meyer, X. Sala, Inorg. Chem. 2013, 52, 6782–6791.
[20] H. Chai, Q. Wang, T. Liu, Z. Yu, Dalton Trans. 2015, 44, 17834–17849.
[21] B. Schäfer, C. Rajnak, M. Ruben, O. Fuhr, D. Klar, C. Schmitz-Antoniai, H. Wende, M. Ruben, Chem. Commun. 2013, 49, 10986–10988.
[22] M. Bõca, R. F. Jameson, W. Linert, Coord. Chem. Rev. 2011, 255, 290–317.
[23] M. Heller, U. S. Schubert, Eur. J. Org. Chem. 2003, 947–961.
[24] A. M. W. Cargill Thompson, Coord. Chem. Rev. 1997, 160, 1–52.
[25] K. Kobayashi, M. Ishikubou, K. Kanaizuka, K. Kosuge, S. Masaoka, K. Sakai, K. Nozaki, M. A. M. Haga, Chem. A Eur. J. 2011, 17, 6954–6963.
[26] M. A. Halcrow, Coord. Chem. Rev. 2005, 249, 2880–2908.
[27] R. Fallahpour, Synthesis (Stuttg. J. 2003, 155–185.
[28] M. A. Halcrow, New J. Chem. 2014, 38, 1868–1882.
[29] M. aki Haga, T. Takasugi, A. Tomie, M. Ishizuya, T. Yamada, M. D. Hossain, M. Inoue, Dalton Trans. 2003, 10, 2069–2079.
[30] J. E. Beves, J. J. Danon, D. A. Leigh, J. F. Lemonnier, I. J. Vitorica-Yzelbab, Angew. Chem. Int. Ed. 2015, 54, 7555–7559; Angew. Chem. 2015, 127, 7665–7669.
[31] J. J. Van Der Vlugt, S. Demeshko, S. Deichert, F. Meyer, Inorg. Chem. 2008, 47, 1576–1585.
[32] T. Bark, M. Duggili, H. Stocek-Evans, A. van Zelewsky, Angew. Chem. Int. Ed. Engl. 2001, 40, 2848–2851.
[33] E. Breuning, M. Ruben, J. M. Leh, F. Renz, Y. Garcia, V. Ksenofontov, P. Gütlich, E. Wegell, K. Rissanen, Angew. Chem. Int. Ed. 2000, 39, 2504–2507; Angew. Chem. 2000, 112, 2563–2566.
[34] B. Schäfer, J.-F. Greisch, I. Faus, T. Bodenstein, I. Salinots, O. Fuhr, K. Fink, V. Schünemann, M. M. Kappes, M. Ruben, Angew. Chem. 2016, 55, 11040–11044.
[35] G. F. Zhang, Z. Q. Chen, M. P. Aldred, Z. Hu, T. Chen, Z. Huang, X. Meng, M. Q. Zhu, Chem. Commun. 2014, 50, 12085–12086.
[36] M. Marschall, J. Reichert, A. Weber-Bargioni, K. Seufert, W. Auwärter, S. Klyatskaya, G. Zoppellaro, M. Ruben, J. V. Barth, Nat. Chem. 2010, 2, 131–137.
[37] P. N. Martino, C. Rajnak, M. Ruben, in Spin-Crossover Mater. Prop. Appl., John Wiley & Sons Ltd, Oxford, UK, 2013, pp. 375–404.
[38] K. Senthil Kumar, M. Ruben, Coord. Chem. Rev. 2017, 346, 176–205.
[39] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.
[40] G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112–122.
[41] G. M. Sheldrick, Acta Crystallogr. Sect. C 2015, C71, 3–8.

Manuscript received: February 23, 2021
Revised manuscript received: March 22, 2021
Accepted manuscript online: March 26, 2021