



## Structural flexibility in complexes bearing a tripodal nitrogen ligand

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### ABSTRACT

Complexes of the divalent metal ions of zinc, cobalt and nickel and a tripodal imidazol-based ligand were investigated for their solution chemistry in protic solvents of varying steric demand. Changes in the coordination number from 4 to 6 are observed depending on solvents, temperature and ions present in solution. With bio-relevant N,O ligands, e.g. amino acids as glycine and alanine, five-coordinate complexes are formed. The solid state structures of the five-coordinate complexes [LNi(H<sub>2</sub>O)Cl]Cl (**3a'**) and [LZn(pic)]NO<sub>3</sub> (L = tris(2-isopropylimidazol-4(5)-yl)phosphane, pic = picolinate) were determined.

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## 1. Introduction

Tripodal nitrogen ligands are widely used as ancillary ligands in catalysis and bioorganic chemistry. The family of hydrotris(pyrazolyl)borates (Tp<sup>R</sup>) are the most prominent of these compounds as they are conveniently prepared and their steric and electronic properties are easily modified [1–6]. Their specific steric and electronic features can be designed by substituents in the 3-, 4- and/or 5-positions of the pyrazolyl rings [3,4]. Especially the substituents in the 3-position can be used to enforce low coordination numbers, e.g. the *tert*-butyl group is regarded as “tetrahedral enforcer” with this respect [7,8]. Ligands with isopropyl substituents also readily form tetrahedral complexes. Sometimes octahedral complexes are obtained by ligand rearrangement of the Tp<sup>R</sup> ligands (Scheme 1) [9] or as with analogous Tpms<sup>iPr</sup> ligands (Tpms = tris(pyrazolyl)methane sulfonato) where N,N,O binding occurs (Scheme 2) [10–12].

Although Tp metal complexes are very good structural compounds for modelling the structure of active sites of metalloenzymes their poor water-solubility limits the usage of Tp metal complexes for modelling the function of those enzymes and furthermore impedes green chemistry applications in water and alcoholic solvents. Another major disadvantage of the Tp-type ligands as well as of the analogous tris(pyrazolyl)methane (Tpm) ligands is their inherent instability in aqueous, more general in protic solvents. Therefore most studies using complexes of these ligands were performed in organic, usually non-coordinating solvents. To improve the solubility in water as the physiologically

relevant solvents charged groups, such as sulfonate, can be used. Anionic groups are often good ligands and can compete with the pyrazole donors and preferentially bind to certain metals, thereby changing the coordination geometry (Scheme 2) [10–15].

The development of water-soluble and stable analogs to the Tp-type scorpionate ligands (Chart 1) is still challenging [10–13,16–26]. We developed a class of ligands where the pyrazolyl are replaced by imidazolyl substituents connected via the 4(5)-position to a phosphorus atom, which replaces the boron atom in the Tp ligands. Alkyl or aryl substituents in 2-position are used to determine the steric demand of these 4-TIP<sup>R</sup> ligands [27,28]. In our experience, 4-TIP<sup>R</sup> complexes behave as κ<sup>3</sup>-N,N,N donors towards 3d metal ions and adopt geometries similar to those seen for Tp complexes. This steric similarity allows for a straightforward prediction of the geometry of the 4-TIP<sup>R</sup> complexes using the vast literature on Tp and its complexes. Enzyme modelling studies with Tp ligands in hydrophobic solvents [29,30] can be modified for the use of 4-TIP<sup>R</sup> ligands in water or alcoholic solvents. Thus, bulky 4-TIP<sup>R</sup> ligands will be ideal for modelling hydrophilic enzyme active sites and studying hydrolytic reactions in water [27].

Here we present a study on the dynamic changes of coordination numbers and geometries of 3d-metal complexes with the hydrolytically inert 4-TIP<sup>iPr</sup> ligand in protic solvents related to their use as metalloenzyme models.

## 2. Experimental

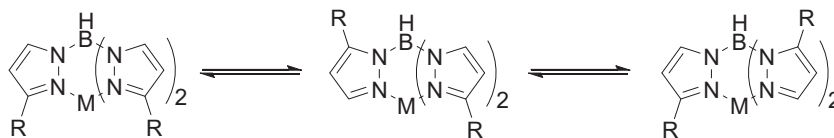
### 2.1. Synthesis

The compounds 4-TIP<sup>iPr</sup>, [(4-TIP<sup>iPr</sup>)Ni(NO<sub>3</sub>)](NO<sub>3</sub>) (**3b**), [(4-TIP<sup>iPr</sup>)CoCl]Cl (**2a**) and [(4-TIP<sup>iPr</sup>)CoNO<sub>3</sub>](NO<sub>3</sub>) (**2b**) were prepared according to a published procedure [28]. All reactions were carried

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<sup>1</sup> X-ray structure analysis.



Scheme 1. Ligand rearrangement in Tp' ligands.

out in Schlenk tubes under an atmosphere of dry nitrogen using anhydrous solvents purified according to standard procedures. All chemicals were purchased from commercial sources and used as received.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker DRX 200 and Bruker DRX 500 spectrometer. The  $^1\text{H}$  spectra were calibrated against the residual proton signal of the solvent as an internal reference ( $\text{CDCl}_3$ :  $\delta_{\text{H}} = 7.30$  ppm; methanol- $d_4$ :  $\delta_{\text{H}} = 3.31$  ppm;  $\text{D}_2\text{O}$ :  $\delta_{\text{H}} = 4.79$  ppm) while the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were referenced to external 85%  $\text{H}_3\text{PO}_4$ . The MALDI mass spectra were recorded on a Bruker Ultraflex MALDI-TOF mass spectrometer using dithranol (DIT) as matrix. The FAB mass spectra were recorded on a mass spectrometer Finnigan, model MAT 8200, in a NBA matrix. Infrared spectra were recorded with a Bruker IFS 66 FT-IR spectrometer. The elemental composition of the compounds was determined with a Perkin Elmer Analyser 2400 at the Institut für Pharmazeutische und Medizinische Chemie, Heinrich-Heine Universität Düsseldorf.

#### 2.1.1. (4-TIP<sup>iPr</sup>)Zn(NO<sub>3</sub>)<sub>2</sub> (**1b**)

4-TIP<sup>iPr</sup> (0.18 g, 50 mmol) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.15 g, 50 mmol) were dissolved in methanol (5 mL) and stirred for 2 h at ambient temperature. Diethyl ether was added and the precipitate filtered off, washed with diethyl ether and dried in vacuo. Yield: 0.16 g (60%) white solid.  $^1\text{H}$  NMR (methanol- $d_4$ ): 1.34 (d,  $J = 7$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 3.42 (sept.,  $J = 7$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 7.53 (d,  $J = 2$  Hz, 1H,  $\text{H}_{\text{im}}$ ),  $^{31}\text{P}\{^1\text{H}\}$  NMR (methanol- $d_4$ ):  $-106$  (HWB = 2 Hz). IR (KBr): 3434 br, 3175 br, 3092 w, 2975 w, 1624 w, 1565 m, 1513 m, 1464 w, 1384 m, 1306 w, 1118 m, 1009 w, 807 w, 745 w, 670 m, 584 w. FAB<sup>+</sup> MS:  $m/z(\%) = 484$  (100)  $[(4\text{-TIP}^{\text{iPr}})\text{Zn}(\text{NO}_3)]^+$ .

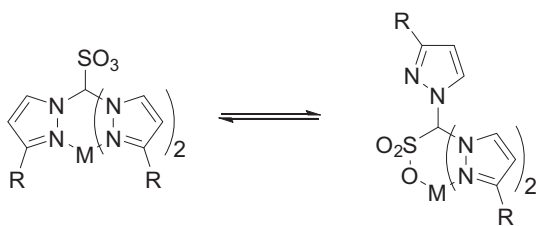
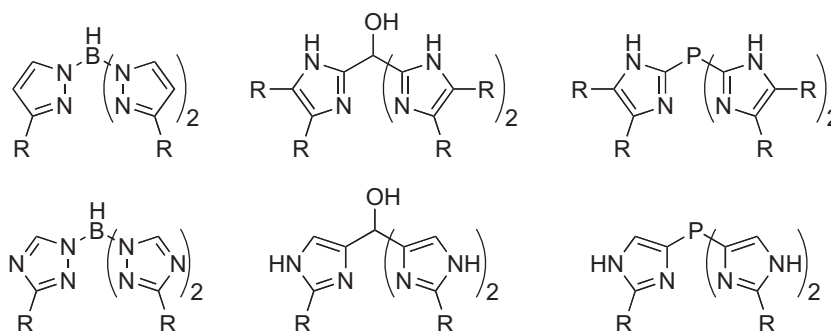
Scheme 2. N,N,N versus N,N,O coordination mode in Tpms<sup>R</sup> ligands.

Chart 1. Tripodal N,N,N ligands.

Anal. Calc. for  $\text{C}_{18}\text{H}_{29}\text{ZnN}_8\text{O}_7\text{P}$  (547.83): C, 38.2; H, 5.2; N, 19.8. Found C, 38.7; H, 4.6; N, 19.4%.

#### 2.1.2. (4-TIP<sup>iPr</sup>)NiCl<sub>2</sub> (**3a**)

4-TIP<sup>iPr</sup> (0.18 g, 50 mmol) and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.12 g, 50 mmol) were dissolved in methanol (5 mL) and stirred for 2 h at ambient temperature. Diethyl ether was added and the precipitate filtered off, washed with diethyl ether and dried in vacuo. The red solid was recrystallized by diffusion of diethyl ether into a solution of **3a** in methanol to yield 0.16 g of a red crystalline solid (62%) which was dried in vacuo.  $[(4\text{-TIP}^{\text{iPr}})\text{NiCl}_2\text{Cl}]$  (**3a**): Slow diffusion of diethyl ether into a solution of **3a** in methanol yielded red crystals of **3a**.  $[(4\text{-TIP}^{\text{iPr}})\text{Ni}(\text{H}_2\text{O})\text{Cl}]$  (**3a'**): Slow diffusion of diethyl ether into a solution of **1** in wet ethanol yielded green crystals of **3a'**.  $^{31}\text{P}\{^1\text{H}\}$  NMR (methanol- $d_4$ ):  $-40$  (HWB = 138 Hz). UV-Vis:  $\lambda_{\text{max}}$  (nm) = 424, 480, 557, 801, 900. IR (KBr): 3381 br, 3143 w, 3076 w, 2970 s, 1622 w, 1561 m, 1508 m, 1463 m, 1437 w, 1392 w, 1367 w, 1310 m, 1243 w, 1162 w, 1118 s, 1066 w, 1029 w, 787 m, 745 w, 670 m, 586 m. FAB<sup>+</sup>-Ms:  $m/z(\%) = 451$  (100)  $[(4\text{-TIP}^{\text{iPr}})\text{NiCl}]^+$ . Anal. Calc. for  $\text{C}_{19}\text{H}_{31}\text{Cl}_2\text{N}_6\text{NiOP}$  (541.13): C, 43.9; H, 6.0; N, 16.2. Found: C, 43.8; H, 5.8; N, 16.5%.

#### 2.1.3. Preparation of 4-TIP<sup>iPr</sup> Complexes with N,O ligands, general procedure

Equivalents of the N,O compound, KO<sup>t</sup>Bu and **1b** or **2b**, respectively, were stirred in methanol (5 mL) for 2 h. The solutions were filtered, diethyl ether (50 mL) added to the filtrate and the organic phase stored at  $-20^\circ\text{C}$  over night. The deposited solid was collected by filtration, washed with diethyl ether, crystallised from acetone / water and dried in vacuo.

2.1.3.1.  $[(4\text{-TIP}^{\text{iPr}})\text{Zn}(\text{pic})]\text{NO}_3$  (**1c**). Yield: 142 mg (74%) white solid.  $^1\text{H}$  NMR (methanol- $d_4$ ):  $\delta$ (ppm) = 1.1 (d,  $J = 7$  Hz, 18 H,  $\text{CH}(\text{CH}_3)_3$ ), 2.9 (quint.,  $J = 7$  Hz, 3H,  $\text{CH}(\text{CH}_3)_3$ ), 7.5 (s, 1H,  $\text{H}_{\text{imidazol}}$ ), 7.7 (t,  $J = 7$  Hz, 1H,  $\text{H}_{\text{pic}}$ ), 8.0 (d,  $J = 7$  Hz, 1H,  $\text{H}_{\text{pic}}$ ), 8.3 (t,  $J = 7$  Hz, 1H,  $\text{H}_{\text{pic}}$ ), 8.5 (d,  $J = 6.7$  Hz, 1H,  $\text{H}_{\text{pic}}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (methanol- $d_4$ ):  $\delta$ (ppm) =  $-105$  (HWB = 5 Hz). IR (KBr): 2980 m, 2971 m, 1564 m, 1462 m, 1419 m, 1413 m, 1381 m, 1168 m, 1140 m, 1130 m, 1106 m, 1074 m, 1003 s, 884 w, 825 m, 781 m, 743 m, 709 m, 658 s, 653 s. MALDI-TOF (MeOH):  $m/z = 575.1$   $[(4\text{-TIP}^{\text{iPr}})\text{Zn}(\text{pic})(\text{MeO})]^+$ , 544.1  $[(4\text{-TIP}^{\text{iPr}})\text{Zn}(\text{pic})]^+$ , 457.0  $[(4\text{-TIP}^{\text{iPr}})\text{ZnCl}]^+$ . Anal.

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