

Syntheses and characterisation of tris(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methane and its bis(μ -hydroxo) dicobalt(II) complex

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Dedicated to Rainer Beckert on the occasion of his 60th birthday

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Abstract

The new ligand tris(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methane (HC(3-Pypz)₃, **1**) has been synthesised by the reaction of 2-(1*H*-pyrazol-3-yl)pyridine with CHCl₃ and Na₂CO₃ under phase-transfer conditions. The reaction of HC(3-Pypz)₃ with Co(BF₄)₂·6 H₂O leads to the formation of dinuclear bis(μ -hydroxo) cobalt(II) complex [Co₂(μ -OH)₂(HC(3-Pypz)₃)₂][BF₄]₂·2MeOH (**2**). This complex was crystallographically characterised. It comprises a Co₂(μ -OH)₂ core with bridging hydroxide ligands. The tripodal tris-(3-(pyridine-2-yl)-1*H*-pyrazol-1-yl)methane ligands coordinate each cobalt atom with one bidentate arm, respectively. By this chelating and at the same time bridging coordination mode an octahedral coordination environment is formed.

Keywords: Tris(pyrazolyl)methane, N donor ligand, cobalt complex, crystal structure, DFT

Introduction

N donor stabilised cobalt complexes have been reported for a multitude of catalytic applications, e.g. as catalysts for industrially useful oxidation processes like the oxidation of alkenes¹ and for various polymerisation processes. The application in polymerisation processes ranges from ethene oligomerisation with iminopyridine cobalt complexes² and propyleneoxide polymerisation with phenoxide Schiff base cobalt complexes³ to the living radical polymerisation of acrylates with tetramesitylporphyrin cobalt systems, which generate stable

radicals.⁴ Furthermore, stoichiometric applications like the transformation of nitriles to aldehydes or cyanides have been subject of considerable interest.⁵

The specific N donor ligand dictates the coordination environment of cobalt and controls its reactivity by its electronic and steric properties. In this context, poly(pyrazolyl)methanes have been studied for decades. The first tris(pyrazolyl)methane was synthesised in 1937 by Hückel and Bretschneider with the reaction of pyrazole potassium salt and chloroform,⁶ but the complicated synthesis hindered its wide application in coordination chemistry. In 1987 Elguero et al. have reported a revised synthesis for tris(pyrazolyl)methanes: in this protocol the pyrazole reacts with chloroform and potassium carbonate under liquid-liquid phase transfer conditions.⁷ By substitution of the base with excess sodium carbonate the yield could be considerably enhanced. A multitude of ligands have been synthesised according to this method, e.g. HC(pz)₃, HC(3,5-Me₂pz)₃, HC(3-Phpz)₃, HC(3-ⁱPrpz)₃ and HC(3-^tBupz)₃.⁸ Beside these tris(pyrazolyl)methanes, a flourishing branch in synthesis and coordination chemistry of *NNO* scorpionate ligands was developed, based on bis(pyrazolyl)methane ligands.⁹

Tris(pyrazolyl)methanes stabilise a great variety of coordination motifs; among these, a facial chelate coordination with local C₃ symmetry represents the most common coordination motif. In many cases, bisfacial wrapping of the metal is observed which can be avoided by using tris(pyrazolyl)methanes of the second generation. These ligands possess a sterically demanding substituent in the 3-position of the pyrazole. In a larger synthetic effort, this 3-position can also be substituted by an additional donor function. For example, Ziessel et al. synthesised in a sophisticated process tris[3-(6-carboxypyridin-2-yl)pyrazol-1-yl]methane with a substituted pyridinyl function in the 3-position.^{10,11} Some years earlier, Ward et al. developed the ligand phenyltris[(3-(2-pyridyl)pyrazol-1-yl)]methane. In this ligand the CH head-group is replaced by a CPh group.¹² In the field of bis(pyrazolyl)methanes, the analogous bis(pyrazolyl)methane (H₂C(3-Pypz)₂) with a pyridinyl function in the 3-position was synthesised by Ward et al. as well.¹³

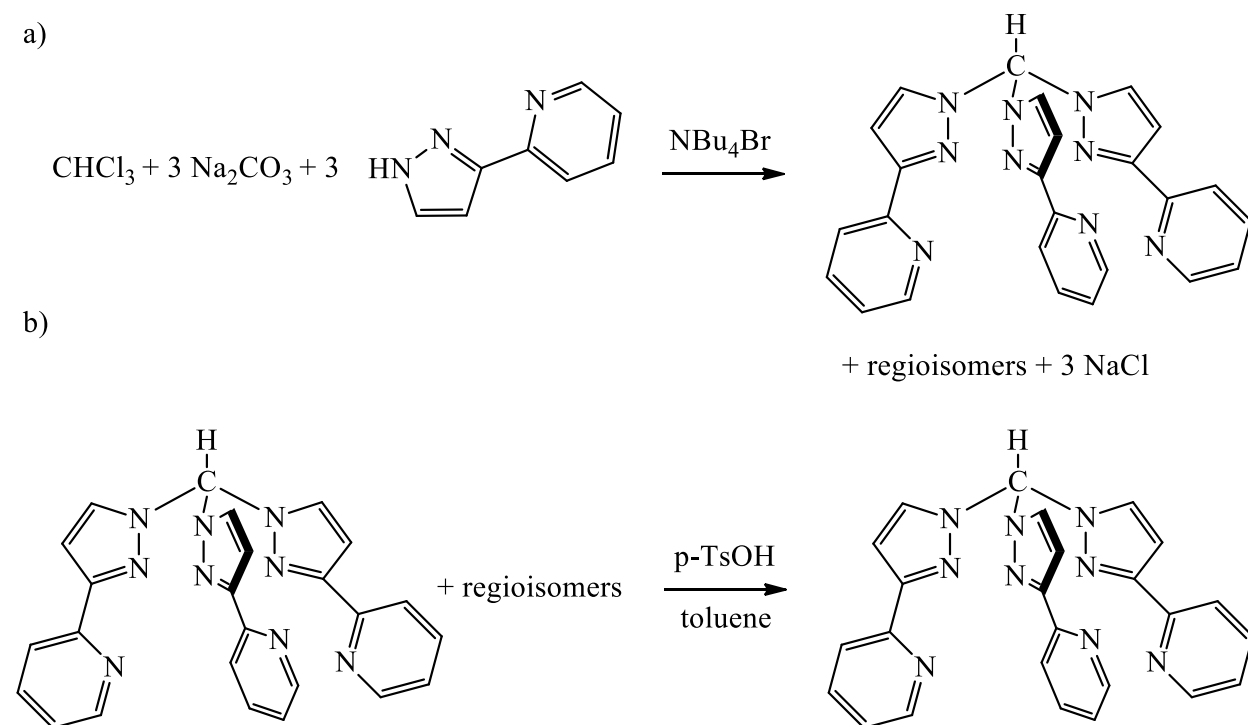
During our synthetic studies on poly(pyrazolyl)methanes,¹⁴ we obtained tris(pyrazolyl)methane tris(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methane (HC(3-Pypz)₃, **1**). Herein we report on the synthesis and characterisation of the new ligand and a structural characterisation of its cobalt(II) bis(μ-hydroxo) dicobalt(II) complex [Co₂(μ-OH)₂(HC(3-Pypz)₃)₂][BF₄]₂·2MeOH (**2**).

Results and Discussion

Synthesis

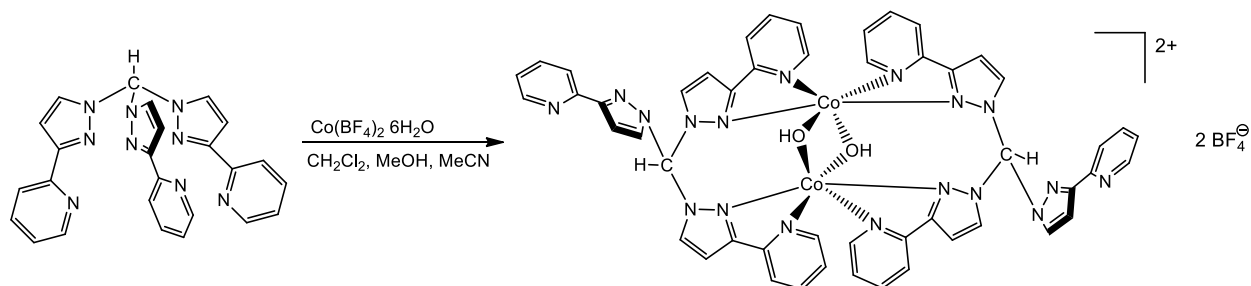
In general, tris(pyrazolyl)methanes are synthesised under liquid-liquid phase transfer conditions by the reaction of the corresponding pyrazole, chloroform and excess base.^{7,8} For the synthesis of the ligand tris(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methane (HC(3-Pypz)₃, **1**) the substituted pyrazole 2-(1*H*-pyrazol-3-yl)pyridine¹⁵ is used (Scheme 1a). With tetrabutylammoniumbromide

as phase-transfer catalyst and sodium carbonate, we obtained the highest yields in this reaction. At first, the pyrazole reacted with the base sodium carbonate in water in an exothermic reaction under presence of the phase-transfer catalyst. After cooling and addition of CHCl_3 to the solution, the reaction mixture was refluxed for three days. After conventional work up, we obtained a mixture of regioisomers of the products in which the pyridinyl function is either in the 3- or in the 5-position. This fact is manifested in the NMR spectra of the crude product which show only a small yield of the desired product. This undesired isomerisation is known and so a further isomerisation step is performed.^{8,10,11} Therefore the mixture of isomers was dissolved in boiling toluene. Addition of a catalytic amount of *p*-toluenesulfonic acid leads to the complete isomerisation of all regioisomers to the desired 3-isomer. Hence, a purification by column chromatography is not necessary (Scheme 1b). The final purification step proceeds as follows: after filtration of the solution at room temperature a red brown precipitate was collected. This precipitate was extensively washed with water, ethanol and hexane to afford the pure ligand tris(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methane ($\text{HC}(3\text{-Pypz})_3$, **1**).



Scheme 1. (a) Synthesis of the ligand $\text{HC}(3\text{-Pypz})_3$ (**1**), (b) Isomerisation of the regioisomers to the desired 3-isomer of the ligand $\text{HC}(3\text{-Pypz})_3$ (**1**).

The complex $[\text{Co}_2(\mu\text{-OH})_2(\text{HC}(3\text{-Pypz})_3)_2][\text{BF}_4]_2 \cdot 2\text{MeOH}$ (**2**, Figure 1) was obtained by mixing equimolar amounts of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile and methanol and the ligand tris(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methane in dichloromethane (Scheme 2). This complex crystallised by gas phase diffusion of diethyl ether.



Scheme 2. Synthesis of the complex $[\text{Co}_2(\mu\text{-OH})_2(\text{HC}(3\text{-Pypz})_3)_2][\text{BF}_4]_2 \cdot 2\text{MeOH}$ (**2**).

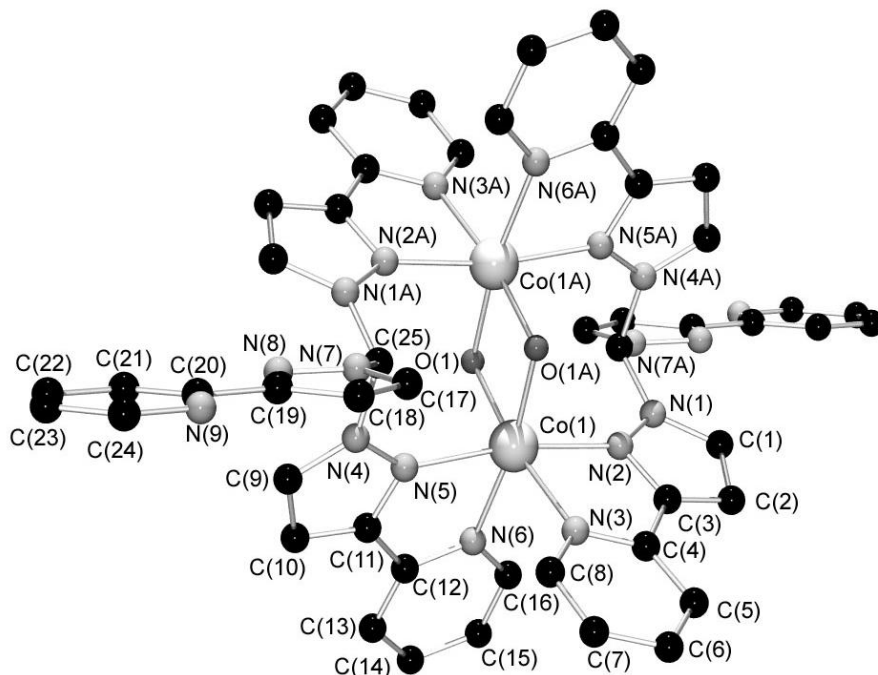


Figure 1. Molecular structure of $[\text{Co}_2(\mu\text{-OH})_2(\text{HC}(3\text{-Pypz})_3)_2]^{2+}$ in crystals of $[\text{Co}_2(\mu\text{-OH})_2(\text{HC}(3\text{-Pypz})_3)_2][\text{BF}_4]_2 \cdot 2\text{MeOH}$ (**2**) (without H atoms).

X-ray crystallography

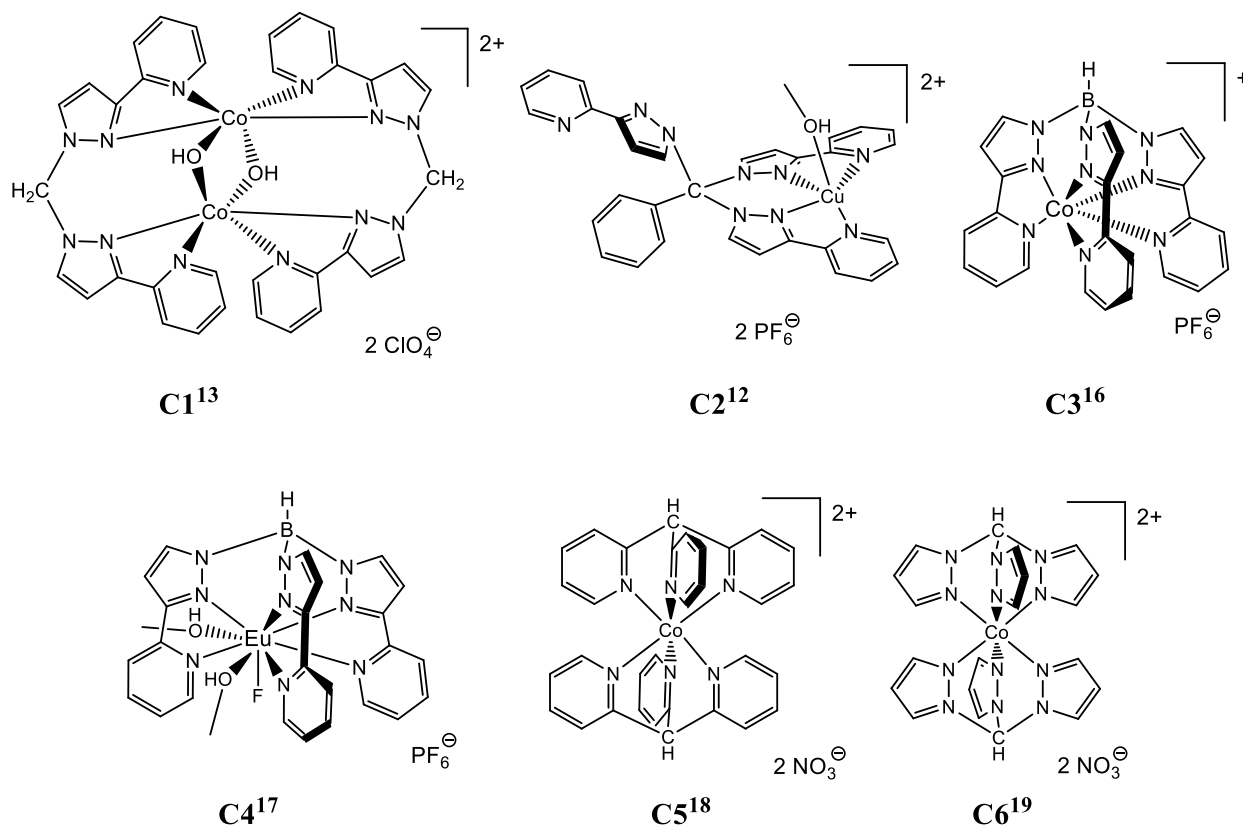
The dinuclear complex compound $[\text{Co}_2(\mu\text{-OH})_2(\text{HC}(3\text{-Pypz})_3)_2][\text{BF}_4]_2 \cdot 2\text{MeOH}$ (**2**, Figure 1) is the first structurally characterised metal complex with tris(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methane, a ligand of the aforementioned second generation. Compound **2** crystallises orthorhombic in the space group *Pbca*. The geometric centre of the cation lies on a crystallographic inversion centre. Figure 1 shows the molecular structure of $[\text{Co}_2(\mu\text{-OH})_2(\text{HC}(3\text{-Pypz})_3)_2]^{2+}$ in crystals of $[\text{Co}_2(\mu\text{-OH})_2(\text{HC}(3\text{-Pypz})_3)_2][\text{BF}_4]_2 \cdot 2\text{MeOH}$. This structure illustrates that each ligand acts as a chelate for each cobalt atom and as a bridge between the cobalt centres, with the two ligands in a non-helical arrangement. Additionally, two hydroxide ions bridge both cobalt centres yielding a $\text{Co}_2(\mu\text{-OH})_2$ rhomb. Each cobalt(II) atom is therefore octahedrally coordinated by two bidentate N pyridinyl/pyrazolyl donor functionalities (one from each ligand)

and two bridging hydroxide oxygen atoms. The third potentially bidentate ligand arm of each of the ligands points into the periphery. The Co-N bond lengths (2.172 – 2.140 Å) are indicative of high-spin cobalt(II) ions. The bond lengths of the cobalt ions to the harder hydroxide ligands are significantly shorter (2.034(1) and 2.044(1) Å). The Co···Co separation amounts to 3.095(3) Å.

Table 1. Selected bond lengths (Å) and angles (°) for the cobalt complexes

	2	C1¹³
Co(1)-O(1)	2.039(2)	2.035(2)
Co(1)-O(1A)	2.044(2)	2.043(2)
Co(1)-N(6)	2.126(2)	2.172(3)
Co(1)-N(5)	2.136(2)	2.172(3)
Co(1)-N(3)	2.140(2)	2.195(3)
Co(1)-N(2)	2.136(2)	2.172(3)
Co(1)-Co(1A)	3.095(1)	2.919(1)
O(1)-Co(1)-O(1A)	81.4(1)	88.6(1)
Co(1)-O(1)-Co(1A)	98.6(1)	91.4(1)
O(1)-Co(1)-N(6)	95.9(1)	93.1(1)
O(1A)-Co(1)-N(6)	170.9(1)	170.9(1)
O(1)-Co(1)-N(5)	93.9(1)	93.4(1)
O(1A)-Co(1)-N(5)	94.2(1)	93.9(1)
N(6)-Co(1)-N(5)	77.2(1)	74.8(1)
N(5)-Co(1)-N(2)	170.4(1)	167.4(1)
O(1)-Co(1)-N(3)	170.9(1)	168.8(1)
O(1A)-Co(1)-N(3)	95.2(1)	94.2(1)
N(6)-Co(1)-N(3)	88.7(1)	85.9(1)
N(5)-Co(1)-N(3)	94.8(1)	96.6(1)
N(2)-Co(1)-N(3)	76.9(1)	75.5(1)

Ward et al.¹³ reported the dinuclear complex [Co₂(H₂C(3-Pypz)₂)₂(μ-OH)₂][ClO₄]₂·MeCN (**C1**, Scheme 3) with the corresponding bis(pyrazolyl)methane as ligand. The ligand H₂C(3-Pypz)₂ contains two pyridinyl/pyrazolyl moieties bridged by a methylene backbone. In this complex each cobalt(II) ion is octahedrally coordinated. Analogously to **2**, both cobalt ions are coordinated by two bidentate pyridinyl/pyrazolyl chelate ligand arms (one from each ligand) and two bridging hydroxide oxygen atoms. The complexes **2** and **C1** show great similarity in their key geometric parameters (Table 2). The Co-O bond lengths for both complexes are equal while the Co-N bond lengths of **2** are significantly shorter. In comparison to **C1** the Co₂O₂ rhomb in **2** is elongated with a O(1)-Co(1)-O(1A) angle of 81.4(1)° (**C1**: 88.6(1)°) and a significant longer Co···Co distance of 3.095(1) Å (**C1**: 2.919(1) Å). So the Co(1)-O(1)-Co(1A) angle in **C1** (91.4(1)°) is smaller than in **2** (98.6(1)°).



Scheme 3. Selected comparative complexes.

The ligand in **C2** (Scheme 3) is similar to the ligand presented herein, but in this ligand the CH head-group is replaced by a CPh group.¹² The copper complex **C2** shows a square-pyramidal coordination environment and the ligand coordinates in a tetradentate manner. The fifth ligand is a solvent molecule. The Cu-N_{py} bond lengths (2.059(3) and 2.051(3) Å) and the Cu-N_{pz} bond lengths (1.944(3) and 1.950(3) Å) are significantly shorter. With the anionic tris(pyrazolyl)borate HB(3-Pypz)₃⁻ the cobalt complex **C3** (Scheme 3) has been reported with a trigonal prism as coordination environment for the cobalt atom.¹⁶ The three Co-N_{py} bond lengths (2.259(5), 2.281(5) and 2.284(5) Å) are considerably longer than the Co-N_{pz} bond lengths (2.060(5), 2.061(5) and 2.066(6) Å). In comparison to **2**, the Co-N_{pz} bond lengths are significantly longer whereas the Co-N_{py} bond lengths are shorter. When the larger europium(III) ion is incorporated into a complex as in the complex cation **C4**, the coordination geometry of europium is mono-capped square antiprismatic (Scheme 3).¹⁷ The three N_{py} donors and both oxygen donor atoms of the solvent describe a pentagonal plane. Also the three N_{pz} donors and one N_{py} donor form one square plane and the next square plane is formed by the two oxygen donors, the fluoride ion and one N_{pz} donor. A N_{py} donor is the cap of the mono-capped square antiprism. The Eu-N_{pz} bond lengths (2.533(11), 2.529(10), 2.551(10) Å) and the Eu-N_{py} bond lengths (2.648(11), 2.659(11), 2.690(10) Å) are larger in comparison to those of **2** as expected for a lanthanide ion with higher

coordination number. In the cobalt complexes with the unsubstituted ligands HC(py)₃ (**C5**) and HC(pz)₃ (**C6**) (Scheme 3),^{18,19} the octahedral coordination environment of the cobalt ion is spanned by Co-N-bond lengths of Co-N_{py} 2.109(2) Å and Co-N_{pz} 2.114(3), 2.108(3), 2.122(2) Å.

DFT calculations

We performed density functional theory calculations taking into account the coordination of the related complex [Co(HB(3-Pypz)₃)] [PF₆] · CH₂Cl₂ (**C3**, Scheme 3).¹⁶ In this complex, the anionic tris(pyrazolyl)borate ligand HB(3-Pypz)₃⁻ stabilises a trigonal prismatic coordinated cobalt ion which we expected for **2** as well.

In principle, the ligand tris(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)methane allows a trigonal prismatic coordination environment, but DFT studies show that the cobalt(II) ion is too small for a trigonal prismatic coordination which is revealed by the Co-N bond lengths of the hypothetical model (BP86/def2-TZVP, Figure 2) with Co-N_{py} 2.141, 2.069 and 3.434 Å and Co-N_{pz} 1.881, 1.884 and 2.376 Å. The system favours a 4+1+1 coordination or after rearrangement an octahedral coordination with bridging ligands.

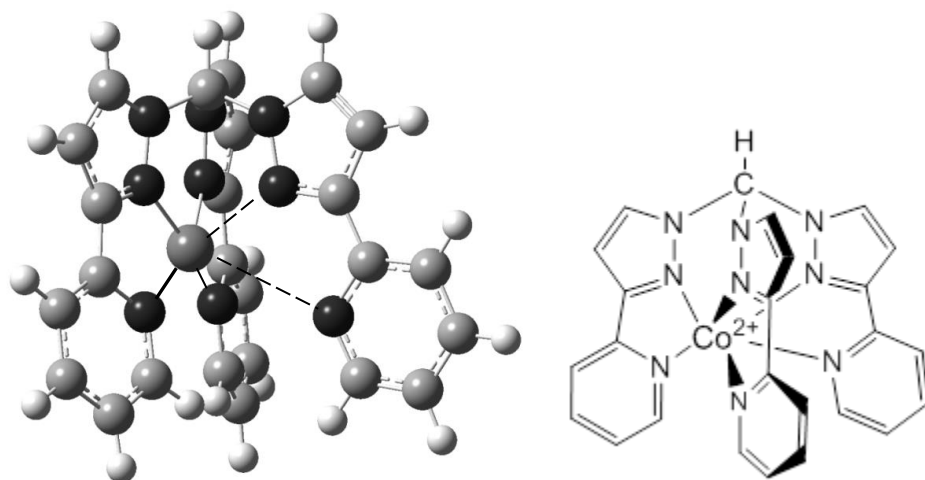


Figure 2. Hypothetical model of a trigonal prismatic coordination.

For a more detailed analysis of the electronic structure of the ligand the Mulliken charges and the NBO charges have been determined. The resulting charges are summarised in Table 2. These charges do not represent absolute charges but the trends give an impression of electronic effects. The advantage of NBO charges over Mulliken charges lies in their greater independence of the basis sets.²⁰ In comparison of pyridinyl functions versus pyrazolyl functions, the pyridinyl donors represent the stronger donor because the charge of the pyridinyl N donor (Mulliken and NBO) is more negative. This is a further argument for the observed coordination in which the pyridinyl donors coordinate closely to the metal.

Table 2. Summary of key geometric parameters of the calculated ligand tris(3-(pyridin-2-yl)-1H-pyrazol-1-yl)methane (HC(3-Pypz)₃) (Gaussian03, RB3LYP/6-31g(d), Mulliken and NBO charges in electron units)

Bond lengths		Mulliken/NBO charges	
d(N=N)/Å	1.351	N _{pz}	-0.341/-0.246
	1.352		-0.350/-0.249
	1.353		-0.399/-0.311
d(C-N _{pz})/Å	1.450	N _{py}	-0.460/-0.429
	1.451		-0.462/-0.430
	1.451		-0.491/-0.454
		C _{ap}	+0.258/+0.325

Conclusions

In this report, we presented the synthesis of the ligand tris(3-(pyridin-2-yl)-1H-pyrazol-1-yl)methane (HC(3-Pypz)₃, **1**) as new member of the family of substituted tris(pyrazolyl)methanes. The synthetic challenge was accomplished by reaction of 2-(1H-pyrazol-3-yl)pyridine with CHCl₃ and Na₂CO₃ under phase-transfer conditions, followed by isomerisation with *p*-toluenesulfonic acid and a purification step. **1** has been used in coordination chemistry and the dinuclear bis(μ-hydroxo) cobalt(II) complex [Co₂(μ-OH)₂(HC(3-Pypz)₃)₂][BF₄]₂·2MeOH (**2**) has been isolated and structurally characterised. The molecular structure shows that each ligand acts as chelate for each cobalt atom and as bridge between the cobalt centres. Additionally, two hydroxide ions bridge both cobalt centres yielding a Co₂(μ-OH)₂ rhomb with octahedral environment for the cobalt atoms. The coordinative potential is now evaluated for further metals.

Experimental Section

General. The substituted pyrazole 2-(1H-pyrazol-3-yl)pyridine was synthesised according to the published procedure.¹⁵ Solvents and other chemicals were commercially available and were used without further purification.

IR spectra were recorded on a Nicolet FT-IR spectrometer P510. ¹H and ¹³C NMR spectra were recorded at 500 and 125 MHz, respectively, on a BRUKER Avance 500 instrument. The NMR signals were calibrated to the residual signals of the deuterated solvents (CDCl₃ δ_H = 7.26 ppm). Mass spectra were recorded on a Finnigan MAT 95 (EI-MS, 70 eV) or on a Finnigan TSQ (ESI-MS). Elemental analyses for C, H and N were obtained using an Elementar analyser vario MICRO Cube (ligand) or a LECO CHNS-932 analyser (complex).

Synthesis of Tris(3-(pyridin-2-yl)-1H-pyrazol-1-yl)methane (1)

2-(1H-Pyrazol-3-yl)pyridine¹⁵ (13.0 g, 90 mmol) and tetra-*n*-butylammonium bromide (1.4 g, 4.3 mmol) were suspended in distilled water (219 ml). With vigorous stirring, sodium carbonate (60 g, 0.56 mol) was added gradually to the reaction mixture. At room temperature chloroform (70 ml) was added and the flask was equipped with a reflux condenser. This mixture was heated at reflux for three days during which it became a dark emulsion. The mixture was allowed to cool to room temperature and filtered to remove the solid sodium carbonate. The organic layer was separated from the aqueous layer and the latter was extracted with diethylether (3×100 ml). The combined organic layers were washed with distilled water (2×200 ml) and dried over sodium sulphate. The solution was filtered and the solvent was removed under reduced pressure. The resulting red-brown residue was dissolved in the minimum amount of hot toluene and poured into a flask containing a small amount of *p*-toluenesulfonic acid (0.18 g). The dark solution was heated at reflux temperature for one day. After it had cooled to room temperature, a dark precipitate appeared that was filtered. The residue was suspended in water (100 ml) and stirred overnight. Then the red brown residue was filtered, washed with water, extensively with ethanol and hexane, to afford pure tris(3-(pyridin-2-yl)-1H-pyrazol-1-yl)methane (HC(3-Pypz)₃, **1**). Sand brown powder, yield 45%, 6.0 g.

¹H NMR (500 MHz, CDCl₃, 25 °C): δ_H 7.03 (3H, d, CH_{pz}, ³J_{HH} = 2.65 Hz), 7.23 (3H, m, CH_{py}), 7.70 (6H, m, CH_{pz} + CH_{py}), 7.96 (3H, d, CH_{py}, ³J_{HH} = 8.0 Hz), 8.60 (1H, s, CH), 8.61 (3H, d, CH_{py}, ³J_{HH} = 5.10 Hz). ¹³C NMR (125 MHz, CDCl₃, 25 °C): δ_C 84.0 (CH), 106.1 (CH_{pz}), 120.6 (CH_{py}), 123.0 (CH_{py}), 130.9 (CH_{pz}), 136.6 (CH_{py}), 149.3 (CH_{py}), 151.2 (C_{py}), 153.9 (C_{pz}). IR (KBr, $\tilde{\nu}$ [cm⁻¹]): 3162 vw (ν(CH_{arom})), 3139 vw (ν(CH_{arom})), 3106 vw (ν(CH_{arom})), 3048 vw (ν(CH_{arom})), 2967 w (ν(CH_{aliph})), 2923 vw (ν(CH_{aliph})), 2852 vw (ν(CH_{aliph})), 1592 s, 1567 m, 1482 vs, 1457 s, 1432 m, 1394 m, 1361 m, 1340 s, 1286 m, 1247 vs, 1213 vs, 1195 s, 1052 m, 1033 m, 812 vs, 802 vs, 792 s, 774 s, 759 vs, 748 m. EI-MS (*m/z*, (%)): 445.1 (35) [M⁺ = C₂₅H₁₉N₉], 303.1 (51) [M⁺-C₈H₆N₃ + 2H], 302.1 (98) [M⁺-C₈H₆N₃ + H], 301.1 (100) [M⁺-C₈H₆N₃], 300.1 (98) [M⁺-C₈H₆N₃ - H], 299.0 (28) [M⁺-C₈H₆N₃ - 2H], 289.1 (5) [C₁₅H₁₁N₇⁺], 288.1 (16) [C₁₅H₁₁N₇⁺ - H], 287 (14) [C₁₅H₁₁N₇⁺ - H], 223.0 (10) [C₁₂H₉N₅⁺], 157.0 (66) [C₉H₇N₃⁺], 156.0 (81), 144.0 (13) [C₈H₆N₃⁺], 143.0 (21), 142.0 (11), 141.0 (4), 80.0 (3), 79.0 (46), 78.0 (94) [C₅H₄N⁺], 76.0 (6). Anal. Calcd for C₂₅H₁₉N₉ (445.1 g/mol): C, 67.40; H, 4.30; N, 28.30%. Found: C, 67.10; H, 4.31; N, 28.00%.

Synthesis of [Co₂(μ-OH)₂(HC(3-Pypz)₃)₂][BF₄]₂·2MeOH (2). Tris(3-(pyridin-2-yl)-1H-pyrazol-1-yl)methane (HC(3-Pypz)₃, **1**, 222 mg, 0.5 mmol) was dissolved in dichloromethane (10 ml). To this solution was added Co(BF₄)₂·6H₂O (170 mg, 0.5 mmol) in acetonitrile (8 ml) and methanol (2 ml). X-ray quality crystals of [Co₂(μ-OH)₂(HC(3-Pypz)₃)₂][BF₄]₂·2MeOH could be obtained by diffusion of diethylether vapour into this solution. Orange crystals, yield: 79 %, 0.25 g. IR (KBr, $\tilde{\nu}$ [cm⁻¹]): 3153 vw (ν(CH_{arom})), 3126 vw (ν(CH_{arom})), 3093 vw (ν(CH_{arom})), 3057 vw (ν(CH_{arom})), 2967 vw (ν(CH_{aliph})), 2923 vw (ν(CH_{aliph})), 2852 vw (ν(CH_{aliph})), 1636 w, 1612 s, 1442 s, 1253 s, 1216 m, 1142 m, 1124 s, 1097 vs, 1083 vs, 1060 vs, 1031 vs, 1013 s. ESI-MS (*m/z*, (%)): 523.1 (6), 522.1 (3), 521.1 (8) [M²⁺ = C₅₀H₄₀Co₂N₁₈O₂/2 = C₂₅H₂₀CoN₉O], 505.1 (5),

504.1 (15) [$M^{2+} - 2 OH$], 503.1 (52), 359.9 (2), 348.0 (10) [$M^{2+} - 2 C_{10}H_8N_2$], 301.1 (43) [$C_{17}H_{13}N_6^+$], 300.1 (4), 289.6 (9) [$C_{15}H_{11}N_7^+$], 272.6 (16) [$C_{10}H_7Co_2N_6^+$], 146.1 (12) [$C_7H_4N_4^+$]. Anal. Calcd for $[Co_2(\mu-OH)_2(HC(3-Pypz)_3)_2][BF_4]_2 \cdot 2MeOH = C_{52}H_{48}N_{18}B_2Co_2F_8O_4$ (1280.56 g/mol): C, 48.77; H, 3.78; N, 19.69%. Found: C, 48.60; H, 3.71; N, 19.60%.

Crystal structure analysis

Crystal data for compound **2** are presented in Table 3.

Table 3. Crystallographic data

2	
Molecular Mass	1280.56
Crystal system	Orthorhombic
Space group	Pbca
a [Å]	14.6715(17)
b [Å]	18.520(2)
c [Å]	20.250(2)
$\alpha = \beta = \gamma$ [°]	90
V [Å ³]	5502.3(11)
Z	4
D _{calc} [g cm ⁻³]	1.546
F(000)	2616
Temperature [K]	120(2)
Θ_{max} [°]	27.88
Reflections collected	41991
Independent reflections	6560
R1 [$I \geq 2\sigma(I)$]	0.0561
wR2 (all data)	0.1385
Largest diff. peak, hole [e Å ⁻³]	0.928 / -0.426

X-ray diffraction data was collected with a Bruker-AXS SMART APEX CCD²¹ using MoK α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Data reduction and absorption correction was performed with SAINT and SADABS.^{21,22} The structure was solved by direct and conventional Fourier methods and all non-hydrogen atoms refined anisotropically with full-matrix least-squares based on F² (SHELXTL^{21,22}). Hydrogen atoms were derived from difference Fourier maps and placed at idealised positions, riding on their parent C atoms, with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(C \text{ methyl})$. All methyl groups were allowed to rotate but not to tip. Besides the BF₄⁻ anions two molecules methanol exist in the unit cell per formula unit in disordered manner. It was possible to model the disordered solvent molecules in an adequate manner, the data set was treated with the SQUEEZE facility of

PLATON.^{23,24} Full crystallographic data (excluding structure factors) for **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC – 742818. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fay: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computational details

Density functional theory (DFT) calculations were performed with the program suite Gaussian 03²⁵ or with the program Turbomole.^{26,27} The geometry of **1** was optimised using the B3LYP^{28,29} hybrid DFT functional and the 6-31g(d) basis set on all atoms as implemented in Gaussian. The Mulliken charge of each atom was calculated by a Mulliken population analysis. The NBO charge of each atom was calculated by a natural bond orbital analysis.^{30,31}

The geometry of the hypothetical model complex was optimised using the BP86 pure functional^{28,32} and the def2-TZVP³³ basis set as implemented in Turbomole on all atoms.

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