



Thermochemistry of a Cobalt Complex with Ionisable Pyrazole Protons

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Abstract: Herein, we present the thermodynamic analysis of a cobalt complex with a new pentadentate N-donor ligand bearing four ionisable pyrazole protons in aqueous solution. A detailed analysis of the Co(II) complex $[Co(L)(X)]^{+/2+}$ in the solid state revealed that the 6th ligand X at the metal centre depends on the cobalt source employed. Small anions such as Cl⁻ and NO₃⁻ coordinate to the metal ion, while larger anions that are weaker hydrogen bond acceptors are found in the second coordination sphere of the complex and instead a solvent molecule coordinates. However, in aqueous KCl solution, the sixth ligand is always chloride forming [Co(L)Cl]Cl, 1^{Cl}. pH dependent species distribution studies revealed a p K_a of 7.3(3) for the first ionisable pyrazole proton in the cobalt (II) complex and 6.0(3) in the cobalt (III) complex (methanol/H₂O mixture). That is the oxidation state has a fairly minor influence on the p K_a of the pyrazole proton. The Co^{III}/Co^{II} redox pair of the complex with the fully protonated ligand exhibits a potential of 0.78 V vs. NHE. The BDFE of the hypothetical H-atom abstraction step of [Co^{III}(L)Cl]⁺ forming [Co^{III}(LH₋₁)Cl]⁺ was determined to equal 336 kJmol⁻¹.

1 Introduction

2 Electron transfer reactions are one of the fundamental reaction types in chemistry. Many, if 3 not most, electron transfer reactions in chemistry and 4 5 biology are coupled to proton transfer events.^[1] For 6 example, multiple site proton-coupled electron 7 transfer (PCET) steps play a crucial role in three out of four oxidation steps in the Kok cycle, that is in the 8 9 water oxidation reaction forming O2 in the photosystem II.^[2] Recently, it has been showed, that 10 metal complexes with ionisable imidazole units have 11 12 an impact on the electrochemical-driven water oxidation catalysis.^[3] Such metal imidazole units 13 14 undergo PCET reactivity and show a thermodynamic coupling between ligand-based proton transfer and 15 metal-based electron transfer.^[4] Very little is known 16 for isoelectronic pyrazole complexes, although 17 18 pyrazoles are also widely used a N-donor moieties in coordination chemistry.^[4i,5] This prompted us to 19 investigate the solution thermochemistry of 20 21 isoelectronic cobalt complex with ionisable pyrazole 22 protons.

23 PCET reactions are usually described by the 24 thermodynamic data of the individual steps, that are 25 the pK_a of the proton transfer step, the redox 26 potential for electron transfer step, and the bond dissociation free energy of the concerted hydrogen 27 28 atom transfer (HAT) step.^[6] According to the thermodynamic square scheme, 29 the bond dissociation free energy (BDFE) of the concerted 30 31 HAT step can be calculated from the thermodynamic 32 data of the individual steps and the H⁺/H[•] standard 33 reduction potential.^[7]

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Metal ion binding to imidazole or imidazole 34 35 containing ligands leads to a decrease of the pK_a of the imidazole protons in comparison to free 36 imidazole and the extend of the effect depends on the 37 38 d-electron configuration of the metal ion.^[3a,8] We 39 expected an even more pronounced effect in an 40 isoelectronic pyrazole complex as the distance 41 between the acidic proton and the cobalt ion is 42 shorter than in the isoelectronic complex $[Co(L^{im})(H_2O)](BF_4)_2$, A^{BF4} (Figure 1).^[9] On the 43 44 other hand, the redox potential of the Co^{III}/Co^{II} redox pair was expected to be higher than in A^{BF4}, because 45 46 imidazole is a stronger σ - and π -donor in comparison 47 to pyrazole.^[10]



49 **Figure 1**. Pentadentate N-donor ligands with ionisable pyrazole 50 or imidazole^[3a] protons.</sup>

51 Results and Discussion

52 Ligand and complex synthesis.

53 L can be synthesised in a 5 step synthesis starting 54 from pyridine-2,6-dicarboxylic acid and pyrazole as 55 shown in Scheme S 1. The synthesis has been adapted from syntheses of similar ligands.^[3a,11] The 56 57 ligand was purified by recrystallisation from ethanol 58 and fully characterised by the usual methods. A 59 single crystal X-ray diffraction experiment affirmed 60 the structure. The result of the refinement is shown 61 in Figure S 1. L crystallises in the orthorhombic 62 space group Fdd2 (Table S 2). The solid state structure shows a hydrogen bond network between 63 two adjacent pyrazole moieties and one ethanol 64 molecule. The distance between the N3...O4 and 65 66 N7...O4 atoms as well as between the N3...O3 and

1 N9...O3 atoms are in the typical range of hydrogen 2 bonds, i.e. ~2.8 Å (Table S 3). The ethanol molecule

3 is bound tightly and cannot be removed under

4 vacuum.

5 The reaction of L and $[Co(H_2O)_6](BF_4)_2$ in methanol

6 led to the complex with the desired structural motif

7 $[CoL(MeOH)](BF_4)_2$, 1^{BF4} (Scheme 1). Mass

8 spectrometry confirmed the composition and

9 elemental analysis the purity of the complex. IR

10 spectroscopy showed a band at 3368 cm^{-1} ,

- 11 indicating that the pyrazole units were still
- 12 protonated.^[12]



13

14 Scheme 1. Synthesis of the cobalt(II) and cobalt(III) complexes.

15 In order to obtain the cobalt(III) complex, L and

16 Co(acac)₃ were heated in HCl-acidified methanol

17 solutions for 5 h. The material, which was obtained,

18 showed a diamagnetic ¹H NMR spectrum indicating

19 the successful formation of [Co(L)Cl]Cl₂, **2**. Indeed,

20 mass spectrometry supported this and elemental

- 21 analysis confirmed the purity of the product.
- 22 Solid state structures.

The structure of 1^{BF4} was confirmed by a single 23 crystal X-ray diffraction experiment. The result is 24 25 shown in Figure 2 and selected bond lengths in Table 1 and angles in Table S 4. 1^{BF4} crystallises in the 26 27 orthorhombic space group $P2_12_12_1$ (Table S 1). The 28 cobalt(II) ion is bound to the ligand in a κ^5 -N₅-mode. 29 The sixth position of the distorted octahedron is occupied by a solvent molecule, i.e. methanol. The 30 31 distances between the equatorial N atoms and the Co 32 ion is shorter than the distances between the axial N 33 atoms and the Co ion. The average N-Co distance of 2.135 Å points to a high spin cobalt(II) ion. The two 34 35 BF₄ anions are captured between two adjacent 36 pyrazole units via hydrogen bonds (Figure S 7). The structure of 1^{BF4} is similar to the one of A^{BF4} . 37 The refinement result of single X-Ray diffraction 38 measurements of A^{BF4} is shown in Figure S 3. A^{BF4} 39

40 crystallises in the orthorhombic space group *Pnma*41 (Table S 2). The cobalt ion has a distorted octahedral

42 coordination geometry and the average N–Co

43 distance of 2.151 Å corroborates the previously

44 reported high spin state (Table 2).^[3a] The octahedral

45 distortion is slightly more prominent in A^{BF4} than in 46 1^{BF4} (Figure S 2 and Figure S 3). The angle between

46 1^{BF4} (Figure S 2 and Figure S 3). The angle between
47 the planes defined by the pyridine ring and the four

48 equatorial nitrogen atoms is 85° in A^{BF4} and 90° in

49 1^{BF4} . The BF₄ anions are bridged between two

50 adjacent molecules of A^{BF4} through hydrogen bonds.



52 **Figure 2.** Molecular structure of 1^{BF4} in the solid state. Most of 53 the hydrogen atoms, two BF_4 anions and one further methanol 54 molecule were omitted for clarity. Thermal ellipsoids are set at 55 the 50% level.

56 Table 1. Selected data for 1 /[Å].

Atoms	1 ^{CI}	1 ^{NO3}	1 ^{BF4}
Co1–N1	2.344(4)	2.2740(16)	2.2255(18)
Co1-N2	2.092(3)	2.1320(16)	2.1188(19)
Co1–N4	2.130(3)	2.1009(17)	2.1083(19)
Co1–N6		2.1015(17)	2.1202(19)
Co1–N8		2.1100(16)	2.1009(19)
ØCo1-N	2.158	2.144	2.135
Co1–X ^{ax}	2.3357(14)	2.0722(14)	2.0161(17)

57 Table 2. Selected data for A, B, and 2^{Cl} /[Å].

Atoms	A ^{BF4}	В	2 ^{CI}
Co1–N1	2.3389(17)	1.979(5)	1.9814(19)
Co1-N2	2.1052(14)	1.956(3)	1.932(2)
Co1–N4	2.1028(14)	1.920(3)	1.908(2)
ØCo1-N	2.151	1.946	1.932
Co1–X ^{ax}	2.087(2)	1.892(5)	2.1841(6)

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59 We employed further cobalt salts such as 60 $[Co(H_2O)_6](Cl)_2$ or $[Co(H_2O)_6](NO_3)_2$ in order to 61 synthesise 1. The single crystal experiments of the 62 respective products showed that the 6th ligand depends on cobalt salt employed. It was methanol in 63 1^{BF4} , a Cl⁻ anion in the experiment employing 64 65 $[Co(H_2O)_6](Cl)_2$ as cobalt source, forming 1^{Cl} , and a nitrate anion in the experiment employing 66 $[Co(H_2O)_6](NO_3)_2$, yielding 1^{NO3}. All derivatives 67 68 have been fully characterised by usual spectroscopic 69 methods and by elemental analysis. The refinement results of the X-Ray experiments are shown in 70 71 Figure S 4 and Figure S 5. 1^{CI} and 1^{NO3} crystallised in the orthorhombic space groups Pnna and Pbca, 72

2

respectively (Table S 1). The bond lengths and the 1 2 overlay of the molecular structures in the solid state show that the bond distances and angles are very 3 similar in the three complexes (Table 1, Figure 3). 4 The average N^{eq}-Co distances of 2.112 in 1^{NO3}, of 5 2.111 Å in 1^{CI}, and of 2.112 in 1^{BF4} are very similar 6 to that of A^{BF4} , but slightly longer than in 7 $[Co(pz_4depy)(H_2O)]^{2+}$ and $[Co(PY5)(H_2O)]^{2+}$ (cf. 8 9 2.067 Å and 2.059 Å, respectively, Py5 = 2,6-(bis(bis-2-pyridyl)-methoxymethane)-pyridine, 10 11 pz4depy = 2,6-bis(1,1-di(1H-pyrazole-1yl)ethyl)pyridine)^[13]. All metal ions show an axial 12 13 distortion, which is more pronounced than in $[Co(pz_4depy)(H_2O)]^{2+}$ (cf. Co-N^{ax} = 2.133 Å)^[13]. 14 15 The nitrate structure also shows a slight equatorial distortion due to hydrogen bonds between two NH 16 pyrazole units and the nitrate ion. The angle between 17 the plane defined by the pyridine ring and the 18 equatorial N₄-plane is 90° in 1^{BF4} and 1^{Cl} , whereas 19 1^{NO3} exhibits an angle of 80° (Figure S 2, Figure S 4, 20 and Figure S 5). 1^{Cl} and 1^{NO3} form an extended 21 22 network in the solid state through hydrogen bonds (Figure S 9, Figure S 10). 23





Figure 3. Overlay of the molecular structures of I^{BF4} (red), I^{NO3}
 (green), and I^{CI}(blue) in the solid state.

A single crystal X-ray diffraction experiment 27 confirmed the structure of 2^{Cl} . The result of the 28 29 refinement process is shown in Figure S 6 and 30 selected bond lengths in Table 2 and angles in Table 31 S 5. 2^{CI} crystallises in the orthorhombic space group 32 $Pna2_1$ (Table S 2). The cobalt ion has a distorted 33 octahedral coordination geometry composed of the 5 N atoms of the ligand and one chlorido ligand. All 34 four pyrazole units are protonated. The distances 35 between the nitrogen atoms and the cobalt ion are 36 37 considerably shorter than in 1 and similar to the 38 distances in $[Co(L^{im})(OH)](Cl)_2$, **B**, which is in line 39 with a low-spin cobalt(III) state. The structure shows a slight equatorial distortion. The angle between the 40 41 plane defined by the pyridine ring and the equatorial N_4 -plane exhibits 82° (Figure S 6), that is, the cobalt 42

- 43 atom is shifted 0.20 Å out of the plane defined by the
- 44 N pyrazole atoms.
- 45 Structure in aqueous solution.

Since the sixth ligand of the cobalt(II) complex 46 47 depends on the cobalt source in the solid state, we 48 investigated the solution structures by paramagnetic 49 ¹H NMR spectroscopy. The proton resonances of the 50 pyridine and pyrazole protons depend on the anion 51 of the cobalt salt. The shifts of the three complexes 52 differ largely in MeOD- d_4 , indicating that the sixth 53 ligand is not substituted by a solvent molecule in 54 solution (Figure S 12). Upon adding 0.1 M potassium 55 chloride to the methanol solutions of 1, the proton resonances of 1^{BF4} and 1^{NO3} shift to the resonances 56 of 1^{Cl} , which confirms initial methanol, NO₃⁻, and 57 58 Cl⁻ binding in 1^{BF4}, 1^{NO3}, and 1^{Cl}, respectively, and chloride binding of the metal ion in the presence of 59 60 ex. KCl (Figure S 13). In methanol/water 80/20 mixtures, the resonance of the protons in 1^{BF4} and 61 1^{NO3} are the same, indicating that the nitrate anion in 62 63 1^{NO3} is substituted by a solvent molecule (Figure S 64 14). Since no solvent molecule was bound in 65 methanol, we assume that water is bound to the metal 66 ion, because it is smaller. The proton resonances in 67 1^{Cl} differ from those of 1^{BF4} , which indicates that the chloride anion is still bound. Upon adding 0.1 M 68 potassium chloride to the methanol/water solutions, 69 the resonances of 1^{BF4} and 1^{NO3} shift to those of 1^{CI} 70 (Figure 4, Figure S 15). That is to say, that the 71 72 $[Co^{II}L(CI)]^+$ cation is present in methanolic and 73 aqueous potassium chloride solution independently 74 of the cobalt salt employed in the synthesis.





78 Subsequently, we investigated the solution speciation in MeOH/H2O (80/20) by titration 79 80 experiments. The ligand was soluble in MeOH/water 81 (80/20) mixtures over the whole pH range of 2-11. 82 Fitting of the UV/Vis data with SPECTFIT^{TM[14]} 83 revealed one protonation equilibrium at pK_a of 3.20 84 (Figure S 16, Table 3). The equilibrium likely 85 belongs to the pyridine unit, because pyridinium has a higher pK_a than pyrazolium due to the repulsion of 86

- two adjacent NH units^[15] (cf. pyrazole $pK_a = 2.49$, 1 pyridine $pK_a = 5.23$ ^[16]. The protonation of the 2 pyrazole units is out of the experimental pH range (< 3 2). In order to corroborate ligand's pK_a , NMR 4 spectra at different pH were recorded.^[17] In line with 5
- the UV/Vis experiment, the pyridine proton 6
- 7 resonances held constant between a pH of 5 and 12,
- and shift to lower field with lower pH of the solution 8
- 9 (Figure S 17, Figure S 18).

Complex formation studies of Co²⁺ ions and L 10 revealed one equilibrium over the pH range of 2-9 11 12 (methanol/water 80/20, I = 0.1 M KCl Table 3). 13 However, the deprotonated complex is not fully soluble and therefore only an approximate pK_a of the 14 15 pyrazole protons can be given. Upon increasing pH, we observe one deprotonation step around a pH of 16 17 7.5 and the analysis of the first derivative of four 18 titration curves led to an average pK_a of 7.3(3) (average of 7.25, 7.25 and 7.50, 7.35). We 19 20 tentatively assigned this to two deprotonation steps, 21 because complexes of the similar ligand Lim and of **L** (see below) showed usually two pK_a at a similar or 22 23 same values. The third and fourth deprotonation step 24 are outside the range of the experiment. The binding 25 of the pyrazole to the metal ion leads to a decrease of the pK_a of the acidic pyrazole proton of about 7 26 27 orders of magnitude (*cf.* pK_a of pyrazole = 14)^[18]. 28 The p K_a of **1** is slightly lower than the one of **A** (*cf*. $pK_a = 9.79^{[3a]}$), which can be rationalised by the 29 shorter distance between the acidic H-atom and the 30 31 metal centre in **1**. The difference in the pK_a of **1** and A is very similar to the difference previously 32 33 observed in isoelectronic copper imidazole and 34 pyrazole complexes.^[4i]

35 **Table 3.** The protonation constants of **L** with Co^{2+} and Co^{3+} ions 36 at 25.0(2) °C, $I = 0.1 \text{ moldm}^{-3}$ (KCl), solvent: methanol/water 37 80/20. Errors of calculated values are given in parentheses.

38 Charges were omitted for clarity.

	L	Co ^{II}	Co ^{III}
pK_a (LH)	3.20(8)		
pK _a (CoLCl)		7.3(3)	6.0(3)
pK_a (CoLH ₋₁ Cl)		7.3(3)	6.7(4)
<u> </u>			. /

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40 Subsequently, we conducted pH-dependent UV-Vis titration 41 experiments employing 2^{Cl} in 42 methanol/water at 0.1 M KCl in order to estimate the

ligand's pK_a in the cobalt(III) complex. The low 43 44 solubility of 2^{CI} in methanol/water mixtures did not 45 allow for NMR or conductivity experiments. Upon 46 increasing the pH, the transition at 270 nm decreases, 47 albeit, only minor changes have been observed 48 (Figure S 20). This is similar to previously investigated copper pyrazole complexes, which also 49 50 showed only minor changes in the UV/Vis data upon deprotonation.^[4i] Fitting of the titration data with 51

SPECTFIT^{TM[14]} led to two pK_a values close to each 52

- other, 6.0 and 6.7.^[19] The two pK_a are ascribed to the 53
- 54 deprotonation of two pyrazole units. The pK_a of the 55 pyrazole protons is similar to the pK_a determined for
- 56 pyrazole in $[(NH_3)Co^{III}(pzH)]^{3+}$ (cf. pK_a = 6.07)^[9a].
- 57 The difference in the pK_a of the oxidised and reduced
- 58 cobalt complex is fairly minor.



60 Figure 5. Species distribution of 2^{Cl} as determined by UV/Vis 61 titration, solvent: methanol/water (80/20); I = 0.1 M KCl.

62 Redox properties.

63 In order to determine the BDFE of the formal Hatom transfer step, we determined the redox potential 64 of the [Co^{III/II}LCl]^{+/2+} redox pair. We collected CV 65 data of 2^{CI} under acidic conditions in order to 66 67 investigate the electron transfer (ET) step at different 68 concentrations and scan rates (Figure 6, Figure S 21).

69 The broad oxidation feature, the separation of the 70 reduction and oxidation waves as well as the peak 71 potential shift with increasing scan rates indicates a 72 rather slow electron transfer rate. This is typical for hs-Co^{II}/ls-Co^{III} redox pairs as the spin state change 73 results in large structural changes.^[13,20] Good fits 74 75 were obtained using reasonable values to describe 76 the redox process. The potential was determined to 77 be $E^{\circ} = 0.78$ V vs. NHE at a rather slow electron 78 transfer rate k_s of 1×10^{-3} cms⁻¹. Representative overlays are depicted in Figure 6 and Figure S 21. 79 The potential of the Co^{III/II} redox pair is slightly 80 81 higher than the one of $[Co(pz_4depy)(H_2O)]^{2+}$ and 82 considerably higher than of **A** due to the weaker σ and π -donor strength of pyrazole in comparison to 83 84 imidazole (*cf*. Ε = 0.63^[13] V in $[Co(pz_4depy)(H_2O)]^{2+}$; $E = 0.51^{[3a]}$ V in A vs. NHE). 85



1

2 Figure 6. CV data of 0.27 mM 2 in MeOH/H₂O 80/20 at pH 2 at 3 rt (0.1 M KCl); black lines: experimental data; red dotted lines: 4 simulation with the parameter values $E_1 = 0.78$ V vs. NHE, $\alpha_1 =$ 5 0.5, $k_s = 1 \times 10^{-3}$ cms⁻¹.

6 Determination of the BDFE.

The BDFE of the hypothetical HAT can be 7 8 determined according to eq. 1, where R is the gas 9 constant, T is temperature, and F is the Faraday constant.^[7a] The first two terms describe the redox 10 potential of the complex and its acid/base 11 12 equilibrium. $c_{\rm G}$ is equivalent to the H⁺/H[•] standard reduction potential in the respective solvent and thus, 13 is independent of the nature of the species 14 involved.^[7] It has been calculated to be 226.3 15 kJmol⁻¹ in MeOH/H₂O 80/20.^[4i] 16

17 BDFE =
$$2.301RTpK_a + FE^0 + c_G(1)$$

18 Based on the thermodynamic data of the various 19 species, i.e. E° , of $[Co^{III/II}(\mathbf{L})Cl]^{2+/+}$, pK_a of 20 $[Co^{II}(\mathbf{L})Cl]^+$, $[Co^{II}(\mathbf{L}H_{-1})Cl]$, $[Co^{III}(\mathbf{L})Cl]^{2+}$, and 21 $[Co^{III}(\mathbf{L}H_{-1})Cl]^+$, we determined a BDFE for the two 22 hypothetical H-atom-abstraction steps of 336 23 kJmol⁻¹ (80.2 kcal mol⁻¹) and 332 kJmol⁻¹ (79.4 kcal

24 mol^{-1}), respectively (Scheme 2).



26 Scheme 2. Thermodynamic square scheme for $1^{Cl}/2^{Cl}$. 27 Thermodynamic values in square brackets have been calculated

28 according to Hess's law.

The reduction potential of the $[Co^{III/II}(LH_{-1})Cl]^{+/0}$ 29 30 redox pair has been calculated to be 0.70 V according to the square scheme formalism, and the 31 32 one of the $[Co^{III/II}(LH_{-2})Cl]^{0/-}$ pair to be 0.67 V.^[21] The protonation state of pyrazole has a fairly minor 33 influence on the redox potential of the Co^{III/II} redox 34 pair in comparison to the potential shift of the Ru^{III/II} 35 36 redox pair in the series of $cis-[(bpy)_2Ru(pzH_{-1})_2]$, 37 and cis-[(bpy)₂Ru(pz)(pzH₋₁)]⁺, cis- $[(bpy)_2Ru(pz)_2]^{2+}$ (cf. 0.54 V, 0.93 V, and 1.42 V vs. 38 NHE, respectively).^[5] In other words, the pK_a of the 39 40 pyrazole unit decreases only slightly by oxidising the 41 metal centre. This could be rationalised by a 42 stabilisation of the protonated cobalt(III) complex 43 via hydrogen bonds to the chloride anions as observed in the solid state structure. This effect is 44 45 likely less pronounced in the cobalt(II) complex, as 46 the complex exhibits a charge of +1 instead of +2 as 47 in **2^{CI}**.

48 In order to substantiate the BDFE, 1 was reacted with 49 a HAT transfer reagent in methanol/water. 4-Dimethylaminophenol (DMAP) has a BDFE of 50 329 kJmol⁻¹ and a p K_a of 10.1 in water, and thus 51 should react with [Co^{III}(LH₋₂)Cl] under H⁺/e⁻-52 53 transfer.^[6] Indeed, UV/Vis-monitoring of the 54 reaction of 10 eq. DMAP and $2^{CI}H_{-2}$ at pH of 9 55 indicates a slow reaction (Figure S 22).^[22] The rather 56 slow reaction can be rationalised by the ls/hs 57 transition upon reduction of the cobalt(III) ion.^[23]

58 Conclusion

59 We synthesised a new ligand with a N₅-donor set and its Co(II) and Co(III) complexes. Characterisation in 60 61 the solid state and solution showed the expected 62 distorted octahedral complexes with the Co(II) ion in 63 high-spin state (1) and the Co(III) ion in low-spin state (2). The sixth ligand in 1 depends on the 64 employed Co(II)-precursor in the solid state and was 65 66 shown to be chloride in solutions with 0.1 M KCl.

67 The pK_a values of the acidic protons in 2 were 68 determined to be 6.0 and 6.7 and were be assigned to 69 the deprotonation of two of the pyrazole units of the 70 ligand, yielding a neutral complex at higher pH. The pK_a of $\mathbf{1}^{Cl}$ was found to be 7.3. This is more than two 71 72 orders of magnitude lower than in A, likely because 73 of the shorter cobalt-NH distance in pyrazole 74 complex compared to imidazole complex. Cyclic 75 voltammetry of 2^{Cl} under acidic conditions revealed 76 a potential of 0.78 V vs. NHE for the Co(II)/Co(III) 77 redox pair. The influence of the oxidation state on 78 the pK_a of ligand in the complex are small compared 79 to previously reported ruthenium complex with 80 pyrazole units, likely due to hydrogen bonding of the 81 anion to the complex. From the thermodynamic data 82 the BDFE for the formal HAT's was calculated to be 336 kJmol⁻¹ and kJmol⁻¹, respectively, which is 83

higher than in a previously reported copper complex
 with pyrazole containing ligands (*cf.* 279
 kJmol⁻¹).^[4i] This shows, that the BDFE can be
 readily tuned by the respective metal/ligand entity,
 which could be exploited in in small molecule
 activation and organic synthesis.^[1e,6,24]

7 Experimental Section

General. Manipulations of air-sensitive reagents 8 9 were carried out in an MBraun glove box, or by 10 means of Schlenk-type techniques involving the use of a dry nitrogen atmosphere. Millipore water and 11 12 methanol were degassed separately by bubbling 13 argon through it before using it. All reagents were 14 purchased as reagent grade or with higher quality and used without further purification. CCDC-15 1837824, CCDC-1837825, CCDC-1837826, 16 17 CCDC-1837827, CCDC-1837829, CCDC-1837829 contain the supplementary crystallographic data for 18 19 this paper. The data can be obtained free of charge 20 from The Cambridge Crystallographic Data Centre 21 via https://www.ccdc.cam.ac.uk/structures/.

22 Complex Synthesis.

1: L (typically 100 mg, 0.19 mmol, 1.00 eq.) and 23 24 $[Co(H_2O)_6]X_2$ (0.19 mmol, 1.00 eq.) were stirred in 25 methanol (3mL) for 2 h. The resulting orange solution was reduced to 1.5 mL, filtered and the 26 27 target compound crystallised by slow diffusion of 28 diethylether. The resulting orange crystal were also 29 suitable for X-ray analysis. The crystals were filtered 30 off and dried in vacuo. Isolated yield typically 31 around 65%.

1^{NO3}: ¹H-PARA-NMR (300 MHz, MeOD- d_4): δ 32 33 (ppm) = 53.5 (2 H, Py-3,5-H), 43.9 (4 H, Pz-H), 34 41.1 (4 H, Pz-H), 17.4 (6 H, OCH₃), 11.1 (1 H, Py-4-H). ESI(+)-MS m/z (%) = 489.1 (20, $[Co(L-H)]^+$), 35 552.1 (76, $[CoL(NO_3)]^+$), 603.1, 1166.2 (14, 36 37 $[Co_2L_2(NO_3)_3]^+$). IR v (cm⁻¹) = 605 (s), 757 (s), 777 38 (m), 1028 (s), 1067 (s), 1123 (s), 1191 (s), 1312 39 (s), 1460 (s), 1521 (s), 1596 (s), 2971 (br), 3422 (br) NO₃-anion: 1384 (s).^[25] Micro analysis (%) 40 41 C₂₁H₂₁N₁₁O₈Co: calc.: C 41.05, 3.45, 25.08; found: 42 C 41.06, H 3.16, N 25.19,.

1^{BF4}: ¹H-PARA-NMR (300 MHz, MeOD- d_4): δ 43 44 (ppm) = 55.5 (2 H, Py-3,5-H), 43.8 (4 H, Pz-H),41.1 (4 H, Pz-H), 18.3 (6 H, OCH₃), 10.8 (1 H, Py-45 46 4-H). ESI(+)-MS m/z (%) = 489.1 (44, $[Co(L-H)]^+$), 47 577.1 (9, $[CoL(BF_4)]^+),$ 603.1 (92). IR $v (cm^{-1}) = 523$ (s), 604 (s), 761 (s), 805 (s), 1127 48 49 (m), 1358 (s), 1454 (s), 1524 (s), 1595 (s), 2951 (br), 50 3368 (br), BF₄-anion: 1071 (s).^[26] Micro analysis (%) C₂₃H₂₉N₉O₄CoB₂F₈: calc.: C 37.94, H 4.01, N 51 17.31; found: C 37.72, H 4.09, N 17.84. 52

53 **1^{CI}**: ¹H-PARA-NMR (300 MHz, MeOD- d_4): δ 54 (ppm) = 54.5 (2 H, Py-3,5-H), 42.1 (4 H, Pz-H), 41.7 (4 H, Pz-H), 17.4 (6 H, OCH₃), 13.8 (1 H, Py-55 4-H). ESI(+)-MS m/z (%) = 229.0 (100, [CoL-56 57 MeOH]²⁺), 245.1 (88, [CoL]²⁺), 432.2 (91), 454.2 58 (80), 489.1 (54, $[Co(L-H)]^+$. IR $v(cm^{-1}) = 608$ (s), 59 760 (s), 781 (m), 795 (s), 1067 (s), 1126 (m), 1196 60 (s), 1225 (s), 1356 (s), 1443 (s), 1454 (s), 1524 (s), 61 1572 (s), 1591 (s), 2953 (s), 3437 (br). Micro 62 analysis (%) C₂₁H₂₃N₉O₃CoCl₂: calc.: C 43.54, H 63 4.00, N 21.76; found: C 43.58, H 3.71, N 21.54.

64 2: L (typically 50 mg, 0.10 mmol, 1.00 eq.) and 65 [Co(acac)₃] (34 mg, 0.10 mmol, 1.00 eq.) were 66 dissolved in methanol (5 mL) and 6 drops of 67 hydrochloric acid (37%) were added. The reaction 68 mixture was heated under reflux for 5 h. 69 Diethylether was added to the solution at ambient 70 temperature, the precipitate was filtered off and 71 washed with diethylether and chloroform several 72 times. Single crystals also suitable for X-ray analysis 73 were obtained by slow diffusion of diethylether into 74 a solution of 2 in methanol. The crystals were filtered 75 off and dried in vacou. Isolated yield typically 76 around 50%.

77 ¹H-NMR (300 MHz, MeOD- d_4): δ (ppm) = 8.36 (dd, 78 J = 7.03 Hz, 1H), 8.27 (d, J = 2.8 Hz, 4H), 8.25 – 79 8.21 (m, 2H), 7.03 (d, J = 2.8 Hz, 4H), 4.28 (s, 6H). 80 $^{13}C{^{1}H}$ - NMR (75 MHz, MeOD- d_4) δ 81 $(ppm) = 160.1 (C_q, Py-2, 6), 151.7 (C_q, Pz-5), 145.1$ 82 (Py-4), 139.3 (Pz-3), 122.9 (Py-3,5), 107.1 (Pz-4), 83 83.6 (Cq, <u>C</u>-OCH₃), 58.1 (OCH₃). ESI(+)-MS m/z 84 (%) = 229.0 (13, [CoL-MeOH]²⁺), 245.1 (12, [CoL]²⁺), 262.5 (44, [CoLCl]²⁺), 524.1 (100, [Co(L-85 H)Cl]⁺. IR v (cm⁻¹) = 608 (s), 716 (s), 748 (s), 779 86 87 (s), 934 (s), 1078 (s), 1138 (s), 1211 (s), 1242 (s), 88 1366 (br), 1458 (m), 1526 (m), 1599 (s), 2916 (br), 89 3430 (br). Micro analysis (%) C₂₁H₂₃N₉O₃CoCl₃: 90 calc.: C 41.03, H 3.77, N 20.51; found: C 41.00, H 3.72, N 20.60. 91

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FULL PAPER

A cobalt complex with a pentadentate N-donor ligand with four ionisable pyrazole units was studied in solid state and solution. The pKa and E° of the individual steps as well as the bond dissociation free energy of the concerted hydrogen atom transfer step were determined.



Thermochemistry

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Thermochemistry of a Cobalt Complex with Ionisable Pyrazole Protons