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## Hydrogen binding in coordination compounds of 3(5)-(4-methoxyphenyl)pyrazole

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#### Abstract

The solid state structures of 3(5)-(4-methoxyphenyl)pyrazole and its coordination compounds with a series of two valent transition metals have been investigated. Since pyrazoles provide not only a nitrogen donor site for the coordination to metal ions, but also an additional N–H function, they are ideal ligands for the formation of hydrogen bound coordination polymers or for the implementation of secondary interactions with other ligands bound to the same central ion, resulting in a rigid ligand environment at the central metal. We chose cobalt, nickel, palladium, copper and zinc as twofold positively charged Lewis acids preferring coordination numbers of four and six to prove the capability of pyrazole to undergo intramolecular hydrogen bonds. In the four-coordinate mode, either tetrahedral  $(Zn^{2+})$  or square planar coordination geometries (Pd<sup>2+</sup>) are possible, providing different geometric restrictions for hydrogen bonding. © 2007 Elsevier B.V. All rights reserved.

Keywords: Pyrazole ligands; Cobalt; Nickel; Palladium; Zinc; Copper; Hydrogen bonds; Crystal structure

## 1. Introduction

At a first glance, the geometry of coordination compounds is determined by the nature of the central ion and the number and the molecular structure of the ligands. However, this definition results from a static view on the shape of these systems, disregarding dynamic processes going on in the ligand sphere. Ligand exchange reactions, which are of severe importance especially for the coordination compounds of main group and f-block elements, lead to a permanent change of the shape. To overcome this and to create complexes of high stability, a multitude of chelating ligands have been introduced into coordination chemistry. But even chelating ligands may undergo rotations of side chains or inversions of the chelating ring system. One further disadvantage of chelating ligands in this context is the reduced solubility of the derived complexes, which is closely related to the reduced mobility. Additionally, more complex procedures are required for the synthesis of chelating compared to monodentate ligands.

A different strategy for the suppression of ligand fluxionality without using chelating ligands is to use, in addition to the metal-ligand interaction, secondary, non-covalent bonds in the ligand sphere of the complex. This will fix the ligands in defined positions at the metal site. One way to do this is to introduce hydrogen bonds in close proximity to the central ion, which can be realized by applying ligands possessing highly polar X-H groups in addition to the donor site. Pyrazole represents a very simple example for such a ligand system. Scheme 1 shows the secondary H-X interaction freezing the rotation around the M-N bond in comparison to the open system with the isomeric imidazole ligand.

Monodentate pyrazoles provide a plethora of different substitution patterns, most of them are not realizable in chelating ligands. Additionally, coordination to a Lewisacidic metal ion will increase the polarization of the N–H bond of the pyrazole and, therefore, increase its capability to be involved in hydrogen binding.

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Scheme 1. Frozen rotation in pyrazole complexes.

Defined and rigid ligand geometries around a metal centre are of special interest for the generation of the so-called metal organic frameworks where (large) multidentate but usually not chelating ligands are used to build up crystalline solids possessing pores like zeolithes [1]. Such materials have attracted the interest due to their special properties, which can be beneficial for catalysis, gas separation and more [2].

In the present publication, we chose an aryl substituted monodentate pyrazole ligand to prove the hypothesis that secondary hydrogen bonds will have a structure-directing influence on the shape of a series of transition metal complexes. For this, we have systematically changed the coordination number and the geometry as well as the nature of the additional anionic ligand for a series of transition metal complexes.

#### 2. Experimental

#### 2.1. General remarks

All starting materials were obtained from ACROS and used without further purification. Elemental analyses were carried out at the Department of Chemistry (TU Kaiserslautern). Infrared spectra were recorded with a FASCO FT-IR 6100 spectrometer. NMR spectra were recorded with a Bruker Avance 400 or 600 spectrometer. The assignment of the NMR data is according to the numbering schemes given below. The resonances of complexes **3** and **4** are assigned according to the numbering of free ligand **2**.

# 2.2. 1-(4-Methoxyphenyl)-3-dimethylaminoprop-2-enone(1)

A mixture of 5.10 g (34 mmol) 4-methoxyacetophenone, 4.05 g (34 mmol) *N*,*N*-dimethylformamide dimethylacetale and 1 ml of triethylamine was heated to 110 °C for 72 h. After cooling to rt 10 ml of Et<sub>2</sub>O was added resulting in the precipitation of the product. The yellow solid was filtered off, washed with *n*-pentane and dried in vacuum. Yield 5.93 g (85%). Mp: 95 °C; *Anal.* Calc. for C<sub>12</sub>H<sub>15</sub>NO<sub>2</sub> (205.26): C, 70.22; H, 7.37; N, 6.82. Found: C, 70.34; H, 7.27; N, 6.60%. <sup>1</sup>H NMR (600 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  2.89, 3.09 (2 × s, 2 × 3H, N(CH<sub>3</sub>)<sub>2</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 5.68 (d, 1H, <sup>3</sup>J<sub>H6,H7</sub> = 12.5 Hz, H6), 6.89 (d, 2H, <sup>3</sup>J<sub>H3,H2</sub> = 8.8 Hz, H3), 7.76 (d, 1H, H7), 7.88 (d, 2H, H2). <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, 25 °C, CDCl<sub>3</sub>)  $\delta$  37.3, 45.0 (N(CH<sub>3</sub>)<sub>2</sub>), 55.4 (OCH<sub>3</sub>), 91.8 (C6), 113.3 (C3), 129.5 (C2), 133.2 (C1), 153.8 (C7), 162.0 (C4), 187.4 (C5). IR (KBr, cm<sup>-1</sup>): 3441 w, 3006 w, 2912 w, 2837 w, 1637s ( $v_{C=0}$ ), 1596 s, 1578 s, 1537 s, 1509 m, 1492 m, 1446 m, 1435 s, 1424 s, 1362 s, 1301 m, 1273m, 1260 s, 1240 s, 1203 w, 1182 w, 1165 m, 1121 m, 1059 m, 1028 w, 1010 w, 957 w, 901 m, 839 m, 820 w, 771 s, 737 w, 685 w, 632 s, 599 m, 516 w, 501 w.



### 2.3. 3(5)-(4-Methoxyphenyl)pyrazole (2)

6.56 g (32 mmol) of 1 and a sixfold excess of hydrazine monohydrate were dissolved in 30 ml of EtOH and heated to reflux for 4 h. After cooling to rt, the volatiles were removed in vacuum. The remaining yellow oil was redissolved in 30 ml of EtOH and the solution was dried over MgSO<sub>4</sub>. The solvent was removed in vacuum to obtain a light yellow solid, which was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> at -20 °C giving colourless crystals. Yield: 5.02 g (90%). Mp: 129 °C. Anal. Calc for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O (174.20): C, 68.95; H, 5.79; N, 16.08. Found: C, 68.88; H, 5.95; N, 16.07%. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>): δ 3.84 (s, 3H, OCH<sub>3</sub>), 6.52 (d, 1H,  ${}^{3}J_{H2,H3} = 2.2$  Hz, H2), 6.92 (d, 2H,  ${}^{3}J_{H6,H5} = 8.8$  Hz, H6), 7.59 (d, 1H, H3), 7.67 (d, 2H, H5), 11.93 (b, 1H, NH).  ${}^{13}C{}^{1}H{}$  NMR (100 MHz, 25 °C, CDCl<sub>3</sub>)  $\delta$  55.5 (OCH<sub>3</sub>), 102.3 (C2), 114.4 (C6), 125.0 (C4), 127.3 (C5), 133.7 (C3), 148.8 (C1), 159.8 (C7). IR (KBr, cm<sup>-1</sup>): 3394 w, 3125 w, 3114 w, 3048 w, 3000 w, 2965 w, 2915 m, 2839 w, 1612 m, 1573 w, 1550 w, 1527 m, 1509 s, 1472 m, 1455 m, 1439 s, 1354 w, 1306 w, 1276 s. 1252 vs. 1183 s. 1114 m. 1097 m. 1055 w. 1028 s. 954 m, 934 m, 896 w, 854 w, 833 s, 809 w, 794 m, 776 s, 674 w, 612 m, 525 m, 438 w.



2.4. [(trans-Dichloro)(bis-5-(4-methoxyphenyl)pyrazole)palladium(II)] (3)

174 mg (1 mmol) of **2** was dissolved in 10 ml of  $CH_2Cl_2$ . To this mixture a solution of 192 mg (0.5 mmol) of  $PdCl_2(PhCN)_2$  in 10 ml of  $CH_2Cl_2$  was added. The resulting orange solution was heated to reflux for 1 h. After cooling to rt an orange microcrystalline solid was obtained. **3**  was recrystallised as orange needles by slow diffusion of npentane into a CH<sub>2</sub>Cl<sub>2</sub> solution. Yield: 258 mg (98%). Anal. Calc. C<sub>20</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Pd (525.53): C. 45.71: H. 3.84: N. 10.66. Found: C, 45.92; H, 4.03; N, 10.82%. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>) δ 3.85 (s, 3H, OCH<sub>3</sub>), 6.35 (t, 1H,  ${}^{3}J_{\text{H2,H3}} = {}^{3}J_{\text{H2,NH}} = 2.2$  Hz, H2), 6.97 (d, 2H,  ${}^{3}J_{\text{H5,H6}} = 8.8 \text{ Hz}, \text{ H6}$ ), 7.46 (d, 2H, H5), 7.97 (t, 1H,  ${}^{3}J_{\text{H3,NH}} = 2.2 \text{ Hz}, \text{ H3}, 11.70 \text{ (s, 1H, NH)}. {}^{13}\text{C}\{{}^{1}\text{H}\}$ NMR (150 MHz, 25 °C, CDCl<sub>3</sub>)  $\delta$  55.8 (OCH<sub>3</sub>), 103.2 (C2), 114.8 (C6), 120.1 (C4), 127.4 (C5), 143.3 (C3), 144.7(C1), 160.9 (C7). IR (KBr,  $cm^{-1}$ ): 3300 s, 3147 w, 2933 w, 2835 w, 1614 s, 1588 w, 1567 w, 1504 vs, 1477 m, 1458 m, 1439 m, 1403 w, 1363 w, 1303 w, 1276 s, 1253 vs, 1182 s, 1137 m, 1117 m, 1091 s, 1080 m, 1058 w, 1031 m, 968 m, 947 w, 886 w, 828 m, 783 s, 723 w, 685 w, 647 w, 635 m, 613 m, 575 w, 550 w, 526 w, 459 w.

## 2.5. [(Dichloro)(bis-5-(4-methoxyphenyl)pyrazole)zinc(II)] (4)

1.39 g (8.0 mmol) of 2 was dissolved in 25 ml of hot EtOH. To this mixture, a solution of 0.55 g (4.0 mmol) of ZnCl<sub>2</sub> in 25 ml of EtOH was added and the resulting clear solution was heated to reflux for 1 h. After cooling to rt, the precipitate was filtered off and dried in vacuum. The product was recrystallized from CHCl<sub>3</sub>/hexanes. Yield: 1.74 g (90%). Anal. Calc. C<sub>20</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Zn (484.64): C, 49.56; H, 4.16; N, 11.56. Found: C, 50.04; H, 4.51; N, 11.11%. <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>): δ 3.84 (s, 3H, OCH<sub>3</sub>), 6.51 (d, 1H,  ${}^{3}J_{H2,H3} = 2.1$  Hz, H2), 6.97 (d, 2H,  ${}^{3}J_{H5,H6} = 8.2$  Hz, H6), 7.60 (d, 2H, H5), 7.84 (s, 1H, H3), 12.69 (b, 1H, NH).  ${}^{13}C{}^{1}H{}$  NMR (100 MHz, 25 °C, CDCl<sub>3</sub>): δ 55.5 (OCH<sub>3</sub>), 103.2 (C2), 114.9 (C6), 120.1 (C4), 127.9 (C5), 141.9 (C3), 145.9 (C1), 161.1 (C7). IR (KBr,  $cm^{-1}$ ): 3530 m, 3415 m, 3236 s, 3149 w, 3004 w, 2961 w, 2932 w, 2835 w, 1616 s, 1589 w, 1573 w, 1511 vs, 1482 m, 1453 m, 1437 m, 1410 w, 1352 w, 1317 m, 1310 m, 1280 m, 1255 vs, 1180 s, 1136 m, 1117 m, 1094 s, 1031 m, 969 m, 945 w, 889 w, 835 s, 797 s, 735 w, 669 w, 611 m, 523 m, 484 w, 467 w, 418 m, 404 m.

## 2.6. [(trans-Dichloro)(tetrakis-5-(4-methoxyphenyl)pyrazole)nickel(II)] (5)

1.39 g (8 mmol) of **2** was dissolved in 25 ml of hot EtOH and a solution of 0.48 g (2 mmol) of NiCl<sub>2</sub> · (H<sub>2</sub>O)<sub>6</sub> in 25 ml of EtOH was added. The resulting clear solution was heated to reflux for 1 h. After cooling to rt dark green crystals of **5** were obtained. They were filtered off, washed with Et<sub>2</sub>O and dried in vacuum. Yield: 1.48 g (90%). *Anal.* Calc. for C<sub>40</sub>H<sub>40</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>4</sub>Ni (822.38): C, 58.42; H, 4.41; N, 13.63. Found: C, 58.18; H, 4.72; N, 13.63%. IR (KBr, cm<sup>-1</sup>): 3265 s, 3228 s, 3001 m, 2960 w, 2928 w, 2832 m, 1613 vs, 1583 w, 1566 w, 1502 vs, 1466 s, 1438 m, 1402 m, 1346 w, 1305 m, 1267 vs, 1250 vs, 1180 s, 1127 s, 1087 vs, 1031 s, 957 vs, 940 s, 889 m, 831 s, 783 vs, 734 w, 724 w, 698 w, 660 m, 635 w, 610 m, 530 m. 2.7. [(trans-Diperchlorato)(tetrakis-5-(4-methoxyphenyl)pyrazole)nickel(II)](6)

174 mg (1 mmol) of **2** and 91 mg (0.25 mmol) of  $Ni(ClO_4)_2 \cdot 6H_2O$  were dissolved in 10 ml of MeOH. The resulting solution was heated for 2 h. After cooling for rt the solvent was removed in vacuum and 6 was obtained as a turquoise solid. Turquoise crystals of 6 were obtained from slow diffusion of n-pentane into a solution of 6 in Yield: 200 mg (84%). Anal. Calc. CHCl<sub>3</sub>. for C<sub>40</sub>H<sub>40</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>12</sub>Ni (954.40): C, 50.34; H, 4.22; N, 11.74. Found: C, 49.77; H, 4.16; N, 11.42. IR (KBr, cm<sup>-1</sup>) 3437 m, 3366 s, 3263 m, 3156 w, 2962 w, 2932 w, 2837 w, 1617 s, 1587 w, 1507 vs, 1475 m, 1441 m, 1404 w, 1351 w, 1308 m, 1278 m, 1256 vs, 1183 s, 1145 s, 1119 vs, 1091 vs, 1031 s, 961 m, 942 w, 918 w, 889 w, 838 m, 788 s, 722 w, 694 w, 663 w, 628 m, 609 w, 526 w.

## 2.8. [(trans-Diperchlorato)(tetrakis-5-(4methoxyphenyl)pyrazole)copper(II)] (7)

174 mg (1 mmol) of **2** was dissolved in 5 ml of MeOH and a solution of 93 mg (0.25 mmol) of Cu(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O in hot water was added. The resulting dark green solution was heated for 1 h. After cooling to rt a brown precipitate was obtained. The precipitate was separated, washed with Et<sub>2</sub>O and dried in vacuum. Brown crystals of **7** were obtained by slow diffusion of *n*-pentane into a solution of **7** in CHCl<sub>3</sub>. Yield 189 g (79%). *Anal.* Calc. for C<sub>40</sub>H<sub>40</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>12</sub>Cu (959.25): C, 50.08; H, 4.20; N, 11.68. Found: 50.08; H, 4.17; N, 11.64%. IR (KBr, cm<sup>-1</sup>) 3350 m, 3286 m, 3151 m, 2935 m, 2838 m, 1750 m, 1616 vs, 1510 vs, 1477 s, 1442 s, 1407 w, 1376 w, 1352 w, 1309 m, 1278 s, 1255 vs, 1184 s, 1132 s, 1120 s, 1094 vs, 1029 m, 965 vs, 945 w, 930 w, 893 w, 836 m, 786 s, 728 w, 694 w, 660 w, 624 m, 526 w.

## 2.9. [(trans-Dichloro)(tetrakis-5-(4-methoxyphenyl)pyrazole)cobalt(II)] (8)

348 mg (2 mmol) of **2** was dissolved in 8 ml of MeOH and a violet solution of 119 mg (0.5 mmol) of  $CoCl_2 \cdot 6H_2O$  in hot MeOH was added. The resulting blue solution was heated to reflux for 2 h. After cooling to rt the solvent was removed. After recrystallization from hot MeOH dark violet crystals of **8** were obtained. Yield 0.39 g (94%). *Anal.* Calc. for  $C_{40}H_{40}Cl_2N_8O_4Co$  (826.65): C, 58.12; H, 4.88; N, 13.56. Found: C, 58.17; H, 4.90; N, 13.66%. IR (KBr, cm<sup>-1</sup>) 3244 s, 3208 s, 3002 m, 2960 w, 2932 w, 2833 m, 2559 w, 2049 w, 1870 w, 1775 w, 1614 vs, 1583 w, 1567 w, 1502 vs, 1468 s, 1438 s, 1402 m, 1346 w, 1306 m, 1269 vs, 1252 vs, 1180 s, 1123 s, 1089 vs, 1033 s, 957 s, 941 s, 892 m, 832 s, 787 s, 725 w, 702 w, 664 m, 611 m, 528 m, 442 w.

#### 2.10. X-ray structure analyses

Single crystals of compounds 2–4 were carefully affixed with an adhesive on to the tips of glass fibers. The crystals

Table 1						
Crystal data and summary	y of intensity	y data collection	and structure	refinement o	of compounds	2-8

Compound	2	3	4	5	6	7	8
Molecular formula	C10H10N2O	$C_{20}H_{20}Cl_2N_4O_2Pd$	$C_{20}H_{20}Cl_2N_4O_2Zn$	C40H40Cl2N8NiO4	C40H40Cl2N8NiO12	C40H40Cl2CuN8O12	C40H40Cl2CoN8O4
Formula weight	174.20	525.70	484.67	826.41	954.41	959.24	826.63
Crystal size (mm)	0.48  imes 0.34  imes 0.20	0.50  imes 0.40  imes 0.20	0.35  imes 0.25  imes 0.20	0.35  imes 0.25  imes 0.20	0.42  imes 0.28  imes 0.12	0.24  imes 0.14  imes 0.08	0.35  imes 0.31  imes 0.26
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	C2/c	$P2_{1}/c$	$P2_{1}/c$	$P2_{1}/c$	$P\overline{1}$	$P\overline{1}$	$P2_{1}/c$
$T(\mathbf{K})$	293(2)	293(2)	293(2)	150(2)	150(2)	150(2)	150(2)
a (Å)	15.7104(10)	14.0458(11)	11.6296(7)	9.9274(2)	12.386(4)	12.241(2)	9.8997(2)
<i>b</i> (Å)	14.8836(11)	11.4707(6)	10.0979(5)	18.4292(3)	13.969(3)	14.076(3)	18.4858(4)
<i>c</i> (Å)	16.7327(10)	13.5608(10)	19.3239(12)	11.1435(2)	14.068(3)	13.952(2)	11.1751(2)
α (°)	90	90	90	90	71.46(2)	72.82(2)	90
β (°)	106.383(7)	107.640(8)	107.102(7)	103.758(2)	67.07(2)	67.28(1)	103.741(2)
γ (°)	90	90	90	90	87.99(2)	86.50(1)	90
$V(Å^3)$	3753.7(4)	2082.1(2)	2169.0(2)	1980.25(6)	2114.4(9)	2114.8(6)	1986.55(7)
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.233	1.677	1.484	1.386	1.499	1.506	1.382
Ζ	16	4	4	2	2	2	2
$\mu_{\rm calc}  ({\rm mm}^{-1})$	0.082	1.172	1.402	2.370	0.658	0.716	0.618
Diffractometer	Stoe IPDS	Stoe IPDS	Stoe IPDS	Oxford Diffr. Gemini S			
				Ultra	Ultra	Ultra	Ultra
Scan type	$\Phi$ oscillation	$\Phi$ rotation	$\Phi$ oscillation	$\Omega$ scans	$\Omega$ scans	$\Omega$ scans	$\Omega$ scans
Radiation	Μο Κα	Μο Κα	Μο Κα	Cu Ka	Μο Κα	Μο Κα	Μο Κα
$\Theta$ range (°)	2.70-26.73	3.04-26.73	2.73-26.73	4.74-62.28	2.67 -32.19	2.67-32.00	2.71-29.99
Reflexions measured	16735	17530	19076	8853	31 044	30.105	18029
Independent reflections	3923	4413	4597	3041	13355	12270	5741
Refined parameters	238	264	264	252	575	575	252
$R^{\rm a}$ (all data)	0.0779	0.0318	0.0362	0.0403	0.1206	0.1006	0.0497
$R^{\mathrm{a}}(I \geq 2\sigma(I))$	0.0390	0.0257	0.0260	0.0332	0.0421	0.0454	0.0321
$wR_2^{b}$ (all data)	0.0992	0.0686	0.0679	0.1079	0.0833	0.0926	0.0800
$wR_2^{b}$ $(I \ge 2\sigma(I))$	0.0904	0.0667	0.0650	0.0898	0.0697	0.0794	0.0742
Goodness-of-fitness <sup>c</sup>	0.809	0.964	0.962	1.127	0.835	0.936	1.037
Residual electron density	0.107/-0.146	0.296/-0.766	0.249/-0.336	0.312/-0.430	0.511/-0.402	0.402/-0.471	0.263/-0.242

 $\frac{(e/Å^{-3})}{{}^{a} R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.}$   ${}^{b} wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum wF_{o}^{2}]^{1/2}.$   ${}^{c} \text{ Goodness-of-fitness} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / (n-p)]^{1/2}.$ 

of complexes 5-8 were immersed in an oil and then attached to the tips of glass fibers. The glass fibers were subsequently mounted on goniometer heads in a nitrogen stream at room temperature or 150 K, respectively. Table 1 summarizes the cell parameters as well as the experimental details of the data collection and the structure refinements of all crystals. In the case of **3**, an analytical absorption correction using ABST from the PLATON program suite was applied [3]. For the other complexes semi-empirical absorption correction was applied using the programs MULABS (for compound 4) and SCALE 3 ABSPACK (for compounds 5-8) from the CrysAlis Red program suite [4]. The structures were solved by direct methods (SHELXS-97) and by Fourier difference maps using the program shelx1-97. The structural parameters were refined by the full-matrix least squares method with the program SHELXL-97 [5]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions using a riding model with isotropic thermal parameters.

## 3. Results and discussion

Aryl substituted pyrazoles can be obtained by a convenient and high yield synthesis starting from commercially available aromatic acetyl derivatives. These compounds undergo a Claisen-type condensation with *N*,*N*-dimethylformamide dimethylacetal to generate 1-aryl-3-dimethylaminoprop-2-enones [6], which can be considered as masked congeners of 1-aryl-1,3-diketones. The derived pyrazoles form instantaneously by reacting the aminopropenones with hydrazine in ethanolic solution [6a]. For the investigation of the coordination behaviour of aryl substituted pyrazoles, we chose the 4-methoxy substituted derivative to enhance the solubility of the complexes in organic solvents, which should also allow a better spectroscopic characterization of the products and in addition facilitate crystallization. The two-step synthesis of 3(5)-(4-methoxyphenyl)pyrazole (2) starts from 4-methoxyacetophenone (4-acetylanisole) and proceeds via 1-(4-methoxyphenyl)-3-dimethylaminoprop-2-enone (1) to the target compound (Scheme 2).

Recrystallization of 2 from  $CH_2Cl_2$  gave crystals of up to 0.5 mm length. Due to the combination of a protondonating and a proton-accepting site in one molecule, it undergoes intermolecular hydrogen binding resulting in a tetrameric structure with  $C_2$  symmetry (Fig. 1). The unit cell contains two crystallographically independent molecules.

The protons in the 12-membered ring, which take part in the hydrogen bonds, are completely disordered according to the N-H tautomerism of pyrazole [7] and its derivatives (see Fig. 1). The observed N···N distances of about 2.85–2.89 Å are typical for N-H···N hydrogen bonds of medium strength [8]. Similar tetrameric arrangements have been found in the solid state structures of a series of pyrazole derivatives [9,10]. All these compounds exhibit a saddle-like structure as it is the case for **2**; however, the curvature of the saddle can differ from an almost coplanar orientation of the four pyrazoles to an arrangement wherein the first and the third as well as the second and the fourth pyrazoles undergo  $\pi$ -stacking with each other.



Scheme 2. (i) Me<sub>2</sub>NCH(OMe)<sub>2</sub>, reflux, 72 h; (ii) N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>O, EtOH, reflux, 4 h.



Fig. 1. Molecular view of the tetrameric arrangement of **2** in the solid state. Selected  $N \cdots N$  distances [Å] in  $N-H \cdots N$  hydrogen bonds:  $N1 \cdots N1' 2.8676(18)$ ,  $N2 \cdots N3 2.8587(19)$ ,  $N4 \cdots N4' 2.8800(19)$ .



Coordination of **2** to a Lewis-acidic metal ion will occur at the sterically less hindered nitrogen atom. Thus, if the pyrazole is not deprotonated, the proton must be shifted to the nitrogen atom next to the pyrazole–phenyl bond, resulting in the formation of the 5-(4-methoxyphenyl)pyrazole tautomer. This is the case for all coordination compounds we have investigated in this series.

The complexes were obtained by stirring an appropriate precursor complex with 2 and 4 equiv. of **2**. With  $PdCl_2(C_6H_5CN)_2$  the pseudo-square planar complex [(*trans*-dichloro)(bis-5-(4-methoxyphenyl)pyrazole)palladium(II)] (**3**) was formed in almost quantitative yields (Scheme 3).

The coordination geometry is typical for a central ion with  $d^8$ -configuration. Recrystallization of **3** gave pale yellow crystals, Fig. 2 shows the molecular structure of **3** in the solid state.

The first remarkable characteristics of this structure are two relatively strong intramolecular hydrogen bonds between the two N–H groups at the pyrazole rings and the two chloro ligands. To optimize the Cl···H–N interaction, the plane defined by N2, N4, Cl1 and Cl2 is twisted by about 22° against the two pyrazole rings. The phenyl and the pyrazole rings in both 5-(4-methoxyphenyl)pyrazole ligands are oriented almost coplanar to each other. Complex **3** gains energy in the solid state structure by the formation of dimers due to weaker secondary intermolecular Pd···N (Pd1···N: 3.5575 and 3.6122 Å) and Cl···H interactions (Cl···H: 2.97 and 2.85 Å) between neighboring molecules. These dimers are arranged in double chains which are interconnected by additional weak  $C-H\cdots O$  and  $C-H\cdots Cl$  contacts.

To the best of our knowledge, only two solid state structures of one compound of the type  $PdCl_2L_2$  (with L = pyrazole with intact N-H function) have been published up tonow [11]. In both cases, 3,5-di(*tert*-butyl)pyrazole was usedas the ligand. This complex crystallizes with the inclusionof either diethylether or dichloromethane in the solid material [12]. In contrast to complex**3**, there is no intramolecu $lar but intermolecular <math>Cl \cdots H-N$  interaction resulting in hydrogen bound dinuclear complexes, which is quite astonishing, since the bulky <sup>t</sup>Bu groups should be unfavourable for such a dimerization.

Reaction of **2** with  $ZnCl_2$  gave [(dichloro)(bis-5-(4methoxyphenyl)pyrazole)zinc(II)] (**4**) (Scheme 4). In the solid state structure, the zinc cation is coordinated by two pyrazole and two chloro ligands in a distorted tetrahedral geometry (Fig. 3).

Since the Cl–M–N angles increase from about 90° for M = Pd to more than 110° for M = Zn, the Cl···H dis-





Fig. 2. Molecular structure of **3** in the solid state presenting the dimers formed by secondary  $Pd \cdots N$  and  $Cl \cdots H$  interactions. Selected distances [Å], angles [°] and torsion angles [°]: Pd-Cl1 2.2966(7), Pd-Cl2 2.2987(7), Pd-N2 2.0090(19), Pd-N4 2.0066(19); Cl1-Pd-Cl2 178.68(2), Cl1-Pd-N2 89.11(5), Cl1-Pd-N4 90.00(5), Cl2-Pd-N2 90.15(5), Cl2-Pd-N4 90.73(5), N2-Pd-N4 178.86(7), Cl1-Pd-N2-N1 -22.96(16), Cl1-Pd-N4-N3 -158.95(16). Selected distances [Å] and angles [°] in the hydrogen bonds: N1-H1 0.86,  $H1\cdots Cl1 2.49$ ,  $N1\cdots Cl1 2.989(2)$ ,  $N1-H1\cdots Cl1 117$ , N3-H3 0.86,  $H3\cdots Cl2 2.60$ ,  $N3\cdots Cl2 3.073(2)$ ,  $N1-H1\cdots Cl1 117$ ,  $N3-H3\cdots Cl2 116$ .



Fig. 3. Molecular structure of **4** in the solid state. Selected distances [Å] and angles [°]: Zn–Cl1 2.2453(5), Zn–Cl2 2.2573(6), Zn–N2 2.0169(15), Zn–N4 2.0260(16), Cl1–Zn–Cl2 113.30(2), Cl1–Zn–N2 112.57(4), Cl1–Zn–N4 103.92(5), Cl2–Zn–N2 103.10(5), Cl2–Zn–N4 110.63(5), N2–Zn–N4 113.63(7). Selected distances [Å] and angles [°] in the hydrogen bonds: N1–H1 0.86, H1···Cl2\* 2.34, N1···Cl2\* 3.1708(15), N1–H1···Cl2\* 162 (for \*: 2 - x, -1/2 + y, 1/2 - z), N3–H3 0.86, H3···Cl1\*\* 2.38, N3···Cl1\*\* 3.2158(14), N3–H3···Cl1\*\* 164 (for \*: 2 - x, 1/2 + y, 1/2 - z).

tances in 4 become too long for intramolecular hydrogen binding. Therefore, intermolecular hydrogen bonds are formed resulting in hydrogen bound polymeric chains along the crystallographic *c*-axis. These chains are linked by additional weak C–H···O interactions. Up to now, only three solid state structures of compounds of the type ZnCl<sub>2</sub>L<sub>2</sub> (with L = pyrazole with intact N–H function) have been published [11]. In one of these compounds, 3amino-5-*tert*-butyl pyrazole was used as the ligand. By involving the amino function of the ligand, a complex three-dimensional network of intra- and intermolecular hydrogen bonds is formed [13]. In the second example, 3,5-di(*tert*-butyl)pyrazole as the ligand gives rise to a dimeric structure, wherein one of the N–H groups forms an intramolecular hydrogen bond with one of the chloro ligands, while the other N–H group undergoes intermolecular hydrogen binding with the chloro ligand, which is not yet involved in the intramolecular hydrogen bridge at the second zinc site [14]. The third example was synthesized by Wagner and Lerner et al. by the  $Zn^{2+}$ -induced cleavage of  $[RB(tBu-pz)_3]^-$ , which seems to be a general route to transition metal pyrazole and pyrazolide complexes [15].



Fig. 4. Molecular structure of **5** in the solid state. Selected distances [Å], angles [°] and torsion angles [°]: Ni–N2 2.090(2), Ni–N4 2.107(2), Ni–Cl1 2.4658(6), N2–Ni–N4 88.69(7), N2'–Ni–N4 91.31(7), N2–Ni–Cl1 89.90(5), N2'–Ni–Cl 90.11(5), N4–Ni–Cl1 90.36(5), N4'–Ni–Cl1 89.46(5). Selected distances [Å] and angles [°] in the hydrogen bonds: N1–H1 0.88, H1···Cl1 2.40, N1···Cl1 3.032(2), N1–H1···Cl1 130.00, N3–H3A 0.88, H3A···Cl1 2.33, N3···Cl1 2.992(2), N3–H3A···Cl1 132.00.



Scheme 5.

This paper presents an interesting overview on a series of such systems although intra-and intermolecular hydrogen binding is not discussed.

Since ligand 2 and complexes 3 and 4 are diamagnetic species, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy allows to assign the electronic situation especially of the pyrazole ring. For the assignment of the NMR data, see Section 2. The differences in the shifts of H6 of the 4-methoxyphenyl ring and the methoxy group are not significant. However, a shift of the resonance of H3 (pyrazole ring) of 0.38 ppm for compound 3 and 0.25 ppm for compound 4 to lower field compared to the resonance of H3 of compound 2 is due to the electron donation from the pyrazole ring to the metal sites. This effect was already observed for pyrazole-containing ligands in other coordination compounds [16]. For the remaining two protons H2 and H5, which are also bound to carbon, the situation is different: while the resonances of these protons are almost similar for 2 and the zinc complex 4, they are shifted by about 0.20 ppm to higher field in the palladium complex 3, indicating an increased shielding in these positions. This could be caused by intermolecular  $\pi$ -stacking [17] or N-H···Cl interactions in solution, which should be possible due to the flat molecular geometry of 3. Even the resonance of the NH function of 3 is shifted to higher field (0.23 ppm compared to 2), while it is strongly shifted to lower field (0.76 ppm) for the zinc complex 4.

In the <sup>13</sup>C NMR spectra of **3** and **4**, the resonance of C3, which is the carbon atom next to the coordinating nitrogen atom in the pyrazole ring, significantly shifts to lower field by 8–10 ppm. This effect again can be explained by the transfer of electron density from the pyrazole to the metal ions. The resonance of the carbon atom C2 is almost unaffected by the coordination, while the resonance of C1 shifts is slightly shifted to higher field, probably due to the complete shift of the N–H proton to the neighbouring nitrogen atom. A similar shift is observed for C4 (at the phenyl ring). All other carbon resonances are unaffected by the coordination.

For the following investigations,  $Ni^{2+}$ ,  $Co^{2+}$  and  $Cu^{2+}$ were chosen which preferentially exhibit octahedral coordination geometries (Scheme 5). This should allow a direct comparison of the effects of intramolecular N–H···X hydrogen bonds on the overall molecular structure as well as on the crystallographic parameters of the derived coordination compounds.

The complex [(*trans*-dichloro)(tetrakis-5-(4-methoxyphenyl)pyrazole)nickel(II)] (5) is obtained by reacting NiCl<sub>2</sub> · (H<sub>2</sub>O)<sub>6</sub> with **2** in EtOH. In the solid state structure, the nickel cation is coordinated by two chloro ligands in *trans* position and four pyrazole ligands (Fig. 4).

Due to the octahedral coordination geometry and the *trans* orientation of the two chloro ligands, all Cl-M-pz



Fig. 5. Molecular structure of **6** in the solid state. Selected distances [Å], angles [°] and torsion angles [°]. Ni1–N2 2.068(2), Ni1–N4 2.060(2), Ni1–O3 2.210(2), Cl1–O3 1.458(2), Cl1–O4 1.432(2), Cl1–O5 1.416(2), Cl1–O6 1.437(2), Ni2–N6 2.074(2), Ni2–N8 2.047(2), Ni2–O9 2.155(2), Cl2–O9 1.439(2), Cl2–O10 1.431(2), Cl2–O11 1.414(2), Cl2–O12 1.422(2), N2–Ni1–O3 86.90(6), N2–Ni1–N4 88.06(7), N2–Ni1–N4' 91.94(7), N2'–Ni1–O3 93.10(6), N4–Ni1–O3 84.67(6), N4–Ni1–O3' 95.33(6), O3–Cl1–O4 108.23(9), O3–Cl1–O5 109.52(10), O3–Cl1–O6 108.89(9), O4–Cl1–O5 111.23(11), O4–Cl1–O6 109.73(11), O5–Cl1–O6 109.20(9), Cl1–O3–Ni1 140.20(9), N6–Ni2–N8 89.95(7), N6–Ni2–N8' 90.05(7), N6–Ni2–O9 87.04(7), N6'–Ni2–O9 92.96(7), N8–Ni2–O9 84.47(7), N8'–Ni2–O9 95.53(7), Cl2–O9–Ni2 155.71(10), O9–Cl2–O10 108.10(11), O9–Cl2–O10 108.81(10), O9–Cl2–O12 107.89(12), O10–Cl2–O1 111.29(10), O10–Cl2–O12 109.14(10), O11–Cl2–O12 111.49(11). Selected distances [Å] and angles [°] in the hydrogen bonds: N1–H1 0.88, H1···O4 2.05, N1···O4 2.917(3), N1–H1···O4 168.0, N3–H3 0.88, H3···O6 2.10, N3···O6 2.866(2), N3–H3···O6 145.0, N5–H5A 0.88, H5A···O12 2.36, N5···O12 3.089(3), N5–H5A···O12 140.00, N7–H7 0.88, H7···O10 2.16, N7···O10 2.908(3), N7–H7···O10 142.00.

angles are found to be about  $90^{\circ}$ , as it was the case for 3. This allows intramolecular hydrogen binding as before. Each of the chloro ligands acts as a proton acceptor for two pyrazole N-H groups. The nickel(II) ions are the centres of inversion in the structure, which leads to a linear arrangement of the complexes along the crystallographic c-axis. According to an inquiry in the Cambridge Structural Database [11], only two solid state structures of complexes of the type  $NiCl_2L_4$  (with L = pyrazole with intact N-H function) have been published up to now. Pyrazole and 3.5-diethyl-4-methylpyrazole have been used in these examples [18]. Similar hydrogen bond patterns as in 5 have been found in both cases. Due to the reduced steric demand of the simple pyrazole ligand in [(trans-dichloro)(tetrakispyrazole)nickel(II)], additional intermolecular N- $H \cdots Cl$  bonds are formed resulting in a linear hydrogen bound polymer.

Formal exchange of the chloro ligands in **5** against perchlorate anions elongates the distance between the protonaccepting site and the central ion without affecting the coordination geometry of the nickel ion. The corresponding nickel complex **6** was obtained by reacting **2** and Ni(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O in MeOH. In the solid state structure, the nickel cation is coordinated by two perchlorato ligands in *trans* position and four pyrazole units. There are two crystallographically different molecules found in the unit cell (Fig. 5).

Since the metal bound oxygen atom of the perchlorate anions is a poor proton acceptor, the N-H units undergo intramolecular hydrogen bonding with two of the noncoordinating oxygen atoms of the perchlorate anions. This implies a twist of the pyrazole groups around the N-Ni bond. While in complex 5 the five-membered rings including the N-H···Cl fragments are almost planar, the corresponding seven-membered rings in 6 are strongly bent out of planarity. There are two molecules in the unit cell that differ in the direction of the rotation of the pyrazoles groups: in one of the complexes, the pyrazoles are rotated in the same direction; (Fig. 5, left) in the second complex, they are rotated in opposite directions (Fig. 5, right). Compound 6 is the first structurally characterized example of a complex of the type  $Ni(ClO_4)_2L_4$  (with L = pyrazole with intact N-H function) [11].

We next moved to the corresponding copper(II) complex. Due to its  $d^9$ -configuration octahedrally coordinated copper(II) will show Jahn-Teller distortion, leading to a slight decrease of the M–N distances but a pronounced increase of the M–O distances. However, if hydrogen bonding is a determining factor for the molecular structures of these complexes, it should have a balancing



Fig. 6. Molecular structure of **7** in the solid state. Selected distances [Å], angles [°] and torsion angles [°]. Cu1–N2 2.002(2), Cu1–N4 2.002(2), Cu1–O3 2.520 (2), Cl1–O3 1.443(2), Cl1–O4 1.427(2), Cl1–O5 1.423(2), Cl1–O6 1.439(2), Cu2–N6 2.011(2), Cu2–N8 1.994(2), Cu2–O9 2.426(2), Cl2–O9 1.430(2), Cl2–O10 1.430(2), Cl2–O11 1.424(2), Cl2–O12 1.429(2), N2–Cu1–N4 88.20(8), N2–Cu1–N4' 91.80(8), N2–Cu1–O3 86.06(7), N2'–Cu1–O3 93.94(7), N4–Cu1–O3 85.49(7), N4'–Cu1–O3 94.51(7), Cl1–O3–Cu1 135.36(10), O3–Cl1–O4 108.00(12), O3–Cl1–O5 110.94(11), O3–Cl1–O6 109.04(12), O4–Cl1–O5 111.03(12), O4–Cl1–O6 109.63(12), O5–Cl1–O6 109.04(12), N6–Cu2–N8 89.82(8), N6'–Cu2–N8 90.18(8), N6–Cu2–O9 87.91(8), N6–Cu2–O9' 92.09(8), N8–Cu2–O9 84.68(8), N8–Cu2–O9' 85.32(8), Cl2–O9–Cu2 151.07(13), O9–Cl2–O10 108.41(13), O9–Cl2–O11 110.69(12), O9–Cl2–O12 107.73(13), O10–Cl2–O11 110.69(12), O10–Cl2–O12 108.38(13), O11–Cl2–O12 111.19(12). Selected distances [Å] and angles [°] in the hydrogen bonds: N1–HN1 0.88, HN1…O4 2.08, N1…O4 2.950(3), N1–HN1…O4 170, N3–H3A 0.88, H3A…O6 2.08, N3…O6 2.868(3), N3–H3A…O6 150.00, N5–H5A 0.88, H5A…O11 2.17, N5…O11 2.935(3), N5–H5A…O11 146.00, N7–H7 0.88, H7…O9 2.56, N7…O9 3.116(3), N7–H7…O9 122.00, N7–H7 0.8800, H7…O10 2.43, N7…O10 3.166(3), N7–H7…O10 141.00.

influence on the overall geometry of the compound. This can clearly be shown for the couple  $Ni(ClO_4)_2(2)_4$  (6) and  $Cu(ClO_4)_2(2)_4$  (7). The latter complex was synthesized by reacting  $Cu(ClO_4)_2 \cdot 6H_2O$  dissolved in hot water with four equivalents of 2 dissolved in MeOH.

The two complexes **6** and **7** are almost isomorphous with respect to their macroscopic crystallographic data: they both crystallize with almost identical cell parameters (Ni/Cu: *a*, 12.386(4)/12.241(2); *b*, 13.969(3)/13.952(2); *c*, 14.068(3)/14.076(3) Å;  $\alpha$ , 71.46(2)/72.82(2);  $\beta$ , 67.07(2)/ 86.50(1);  $\gamma$ , 87.99(2)/67.28(1)°; *V*, 2114.4(9)/2114.8(5) Å<sup>3</sup>; *D*, 1.499/1.506 g cm<sup>-3</sup>). Both structures include two crystallographically different molecules. However, as predicted by electronic considerations, the bond lengths between the central ions and the ligands are strongly different (Ni/Cu: M–N 2.06/2.00 M–O 2.21/2.52 Å). These effects are compensated by comparable parameters of the intermolecular hydrogen bonds (Fig. 6).

There is only one structurally characterized compound of the type  $Cu(ClO_4)_2L_4$  (with L = pyrazole with intact N-H function) [11]. In this publication, 3(5)-*tert*-butylpyrazole was used as the ligand, coordinating to copper(II) via N1 as the sterically favoured 2*H*-3-*tert*-butyl tautomer [19]. Here both the perchlorate anions and the *tert*-butyl groups are disordered, which prevents a structural comparison with complex **7**.

As a final example, we chose cobalt(II) as the central ion. Reacting two equiv. of **2** with CoCl<sub>2</sub> · 6H<sub>2</sub>O in MeOH gives CoCl<sub>2</sub>(**2**)<sub>4</sub> (**8**), which crystallizes in an isomorphic manner to the corresponding nickel(II) complex **5**. As for the couple, **6** and **7** the cell dimensions of **5** and **8** are almost identical (Ni/Co: *a*, 9.9274(2)/9.8997(2); *b*, 18.4292(3)/18.4858(4); *c*, 11.1435(2)/11.1751(2) Å;  $\beta$ , 103.758(2)/103.741(2)°; *V*, 1980.25(6)/1986.55(7) Å<sup>3</sup>; *D* 1.386/1.382 g cm<sup>-3</sup>), which was expected, since there is no big difference in the radii of cobalt(II) and nickel(II) (Ni/ Co: M1–N2, 2.088(2)/2.1168(11); M1–N4, 2.107(2)/ 2.1381(11); M1–Cl1, 2.4648(7)/2.5259(3)). Additionally, the N–H···Cl hydrogen bonds determine the shape of the molecule (Fig. 7).

In the Cambridge Structural Database, there are only two compounds of the type  $CoCl_2L_4$  (with L = pyrazole with intact N–H function) [11]. One is the yet unpublished complex with 2-hydroxy-5-methyl pyrazole, where the chloro ligands are acting as proton acceptors for two N– H and two OH groups. The second is the complex with unsubstituted pyrazole [20]. This compound is again isomorphous to the corresponding nickel(II) complex [18b] and is thus exhibiting the same pattern of intramolecular hydrogen bonds as **8**.

Infrared spectroscopy can give an idea about the strength of the intra- and intermolecular hydrogen bonds. For the free ligand 3(5)-(4-methoxyphenyl)pyrazole (2), an absorption at  $3394 \text{ cm}^{-1}$  was assigned to the N–H stretching vibration, indicating the presence of strong N–H bonds and thus relatively weak intermolecular hydrogen bonds in the tetrameric structure. This corroborates with



Fig. 7. Molecular structure of **8** in the solid state. Selected distances [Å], angles [°] and torsion angles [°]: Co1–N2 2.1170(12), Co1–N4 2.1381(11), Co1–Cl1 2.5258(3), N2–Co1–N4 88.77(4), N2′–Co1–N4 91.23(4), N2–Co1–Cl1 90.67(3), N2′–Co1–Cl1 89.33(3), N4–Co1–Cl1 91.21(3), N4′–Co1–Cl1 88.79(3), N2′–Co1–Cl1 89.73(3). Selected distances [Å] and angles [°] in the hydrogen bonds: N1–H1 0.88, H1···Cl1 2.39, N1···Cl1 3.0454(13), N1–H1···Cl1 131.0, N3–H3A 0.88, H3A···Cl1 2.33, N3···Cl1 3.0044(12), N3–H3A···Cl1 133.00.

the data of the perchlorate complexes **6** and **7**, where the asymmetric and the symmetric N–H absorptions are found at 3366 and 3263 cm<sup>-1</sup> for the nickel(II) complex **6** and at 3350 and 3286 cm<sup>-1</sup> for the copper(II) complex **7**. The palladium complex **3** shows one N–H absorption at 3300 cm<sup>-1</sup>, indicating a weaker N–H and thus a stronger H···Cl interaction. Even more weak N–H bonds and thus stronger H···X bonds are found for the tetrahedral and octahedral chloro complexes **4** (Zn,  $v_{\rm NH}$ : 3236 cm<sup>-1</sup>), **5** (Ni,  $v_{\rm NH}$ : 3265, 3228 cm<sup>-1</sup>) and **8** (Co,  $v_{\rm NH}$ : 3244, 3208 cm<sup>-1</sup>).

## 4. Conclusion

By the reaction of 3(5)-(4-methoxyphenyl)pyrazole (2) with two valent transition metal chlorides, a series of pyrazole complexes could be synthesized. In all cases, intraor intermolecular hydrogen bonding between the pyrazole N–H group and the anionic ligands coordinated to the central ion results in the formation of rigid though well-soluble structures. We are now going to extend this strategy to systems which can be used as building blocks for (porous) coordination polymers. This can be done by attaching a further anionic group (e.g. a carboxylate or sulfonate function) to the phenyl ring of the phenyl pyrazole in combination with kinetically inert pyrazole complexes like **3**.

#### Appendix A. Supplementary material

CCDC 667508, 667509, 667510, 667511, 667512, 667513 and 667514 contain the supplementary crystallographic data for **2**, **3**, **4**, **5**, **6**, **7** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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