DOI: 10.1002/ejic.200700313

Coordination Versatility of 5(3)-(2-Hydroxyphenyl)-3(5)-methylpyrazole: Synthesis, Crystal Structure and Properties of Co^{III}, Ni^{II} and Cu^{II} Complexes

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Keywords: Cobalt / Nickel / Copper / Pyrazoles / Phenols / Crystal structures

New complexes with 5(3)-(2-hydroxyphenyl)-3(5)-methylpyrazole (H_2phpz), $[Co_2(H_2phpz)(Hphpz)_2(phpz)_2]\cdot 3CH_3CN$ (**1**), $[Ni(Hphpz)_2]$ (**2**) and $[Cu(Hphpz)_2]$ (**3**), were synthesized and structurally characterized. The ligand coordinates in the form of 3-(2-hydroxyphenyl)-5-methylpyrazole in all cases, except for one ligand in the Co^{III} complex, where it coordinates in the 5-(2-hydroxyphenyl)-3-methylpyrazole mode. Crystallographic analysis revealed that **1** contains two chemically and crystallographically distinct cobalt(III) ions triply bridged by one phenoxide and two pyrazolate groups, giving rise to a $[Co_2(N\text{-}N)_2O]$ core with a Co···Co distance of 3.154 Å. Additionally, the H_2phpz ligand shows four different coordination modes with the metal ions, demonstrating its versatility. The dinuclear unit of **1** is stabilized by strong intramolecular N–H···O hydrogen-bonding interactions involving the phenol oxygen atom of the H_2phpz ligand and the N–H functionality of the pyrazole ring. The crystal structure of the isomorphous complexes **2** and **3** reveals the presence of centrosymmetric mononuclear units with the MN_2O_2 [M = Ni^{II} (**2**), Cu^{II} (**3**)] chromophore displaying a slightly distorted square-planar geometry. The mononuclear structures of **2** and **3** are further stabilized by intramolecular hydrogen bonds established between the acid N–H group as donor and the phenoxide group of the H_2phpz ligand as acceptor. Spectroscopic studies, ESI-MS and cyclic voltammetry were performed, supporting the crystallographic analysis.
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Introduction

Pyrazole-based ligands have received a great deal of attention over the last decades because of their interesting coordination chemistry, unusual structural features, and remarkable physical and chemical properties.[1,2] The incorporation of pyrazole groups in the design of new ligands allows the study of their structural properties to serve specific stereochemical requirements for a particular metal-binding site. In addition to its remarkable capacity to coordinate to a variety of metal ions, the pyrazole entity also has the ability to bring two metal centres into close proximity and provide an intramolecular pathway for spin-exchange interactions.[3] Although a significant number of coordination compounds containing pyrazole ligands have been obtained to date, the design and synthesis of novel pyrazole-containing complexes by employing more versatile ligands or by varying the nature of the reactants and synthetic conditions are still under investigation. We have recently reported that the ligand 5(3)-(2-hydroxyphenyl)-3(5)-methylpyrazole (H_2phpz) exhibits a variety of coordination abilities and tends to form large metal cluster aggregates.[4,5] The amount of base or the type of solvent are paramount in controlling the different coordination modes, thereby providing a rich versatility to the ligand.

In the present study we extended our investigations to the coordination of this ligand with cobalt, nickel and copper ions, and we report the synthesis, characterization and crystal structure of a quite unusual dinuclear cobalt(III) complex, $[Co_2(H_2phpz)(Hphpz)_2(phpz)_2]\cdot 3CH_3CN$ (**1**), triply bridged by one phenoxide and two pyrazolate groups, as well as two new isomorphous mononuclear complexes $[Ni(Hphpz)_2]$ (**2**) and $[Cu(Hphpz)_2]$ (**3**), and a dopant of Cu^{II} in **2**. To the best of our knowledge, **1** is the first example of a dinuclear cobalt(III) complex bridged by both pyrazolate and phenoxide groups. A remarkable feature of this compound is the observed binding versatility of the H_2phpz ligand, which is coordinated in four different modes to the two cobalt(III) ions (Scheme 1).

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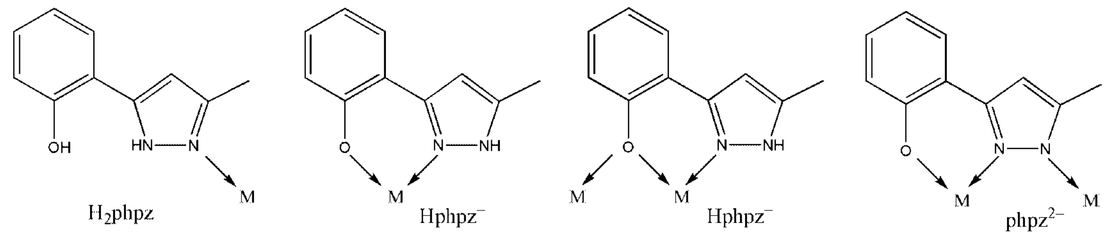

Scheme 1. Four different coordination modes of the 5(3)-(2-hydroxyphenyl)-3(5)-methylpyrazole ligand in complex **1**.

Results and Discussion

Synthesis and Spectroscopic Properties

The reaction of 5(3)-(2-hydroxyphenyl)-3(5)-methylpyrazole (H_2phpz) with $Co(ClO_4)_2{\cdot}6H_2O$ in the ratio 2:1 in the presence of 2 equiv. triethylamine yielded the diamagnetic cobalt(III) complex $[Co_2(H_2phpz)(Hphpz)_2(phpz)_2]{\cdot}3CH_3CN$ (**1**) as a purple solid. After filtration, slow evaporation of the solution afforded dark-brown crystals suitable for X-ray crystallography. The presence of base as well as the aerobic conditions are responsible for the oxidation of cobalt(II) to cobalt(III). The infrared spectrum of **1** suggests the coordination of the ligand to the cobalt(III) ion, as indicated by the shift of the $\nu_{C–O}$ stretching vibration from 1636 cm^{-1} in the free ligand to 1596 cm^{-1} in the complex and the $\nu_{C=N}$ stretching vibration from 1576 cm^{-1} in the free ligand to 1558 cm^{-1} in the complex. The peak observed at 3425 cm^{-1} can be assigned to the phenol hydrogen atom of the H_2phpz ligand that remains neutral by coordination to cobalt(III). The band due to $\nu_{N–H}$ stretching vibration is observed at 3280 cm^{-1} and is less broad than that of the free ligand because of the coordination of the ligands in the complex.[6] The ligand field spectrum of **1** in the solid state exhibits a broad absorption band at 576 nm that is characteristic of octahedral cobalt(III) complexes. The band at 335 nm can be assigned based on its intensity to a $p_\pi \rightarrow d_\sigma^*$ transition, whilst the band at 271 nm arises from a π-π^* ligand transition.[7]

The reaction of $Ni(ClO_4)_2{\cdot}6H_2O$, H_2phpz and Bu_4NOH in a 1:1:2 ratio in methanol yielded a green compound that upon dissolution in dichloromethane followed by slow diffusion of diethyl ether afforded complex **2** as dark-green crystals. The infrared spectrum of **2** displays a strong band assignable to the $\nu_{N–H}$ stretching vibration at 3299 cm^{-1}. Several sharp weak bands observed in the range 2900–3150 cm^{-1} are likely to be caused by the $\nu_{C–H}$ stretches of the methyl group. As the free H_2phpz ligand displays the $\nu_{C–O}$ stretching vibration at 1636 cm^{-1}, the shift of this band to 1600 cm^{-1} in complex **2** suggests the coordination of the phenol oxygen atom. The ligand field spectrum of **2** displays two broad bands at 490 and 622 nm assigned to d-d transitions for the low-spin Ni^{II} compound; the absorption band at 622 nm is assigned to a $d_{x^2-y^2} \rightarrow d_{zy}$ transition, whilst the absorption band at 490 nm is attributed to the $d_{z^2} \rightarrow d_{zy}$ transition.[8] The absorptions observed in the range 420 to 270 nm are likely to be caused by the metal-to-ligand and inter- or intra-ligand charge-transfer transitions. The solid compound turned out to be diamagnetic as expected for square-planar Ni^{II}, thereby allowing the study of a solid solution (dopant) of the isomorphous Cu^{II} compound.

Complex **3** was obtained by reaction of $Cu(ClO_4)_2{\cdot}6H_2O$ and H_2phpz in a 1:1 ratio and in the presence of 2 equiv. sodium methoxide as base. The reaction of H_2phpz with $Ni(OAc)_2$ and $Cu(OAc)_2$ in acetonitrile and in the absence of base afforded **2** and **3**, respectively, as polycrystalline samples with yields up to 76% for **2** and 72% for **3**. The infrared spectrum of complex **3** is very similar to that of complex **2**, and it exhibits the bands expected for the monoanionic Hphpz$^-$ ligand. Notably, the stretching vibrations $\nu_{C–O}$ at 1599 cm^{-1} and $\nu_{C=N}$ at 1548 cm^{-1} are observed at lower energies compared with the IR spectrum of the pure ligand. The ligand field spectrum shows a broad asymmetric band at 660 nm attributed to d-d transitions of copper(II) complexes with square-planar geometry; the absorption bands in the range 455–350 nm are a result of Cu–O and Cu–N charge-transfer transitions.

Description of the Crystal Structures

A single-crystal X-ray analysis of **1** revealed the identity of the product as $[Co_2(H_2phpz)(Hphpz)_2(phpz)_2]{\cdot}3CH_3CN$. Selected bond lengths and angles for **1** are given in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for the complex $[Co_2(H_2phpz)(Hphpz)_2(phpz)_2]{\cdot}3CH_3CN$ (**1**).

Bond lengths			
Co1–O21	1.865(4)	Co2–N11	1.929(5)
Co1–N12	1.875(5)	Co2–O41	1.879(4)
Co1–N31	1.925(6)	Co2–N32	1.875(6)
Co1–O81	1.919(4)	Co2–O61	1.916(4)
Co1–N72	1.914(5)	Co2–N52	1.893(5)
Co1–N91	1.969(6)	Co2–O81	2.002(4)
Co1···Co2	3.154		
Bond angles			
Co1–O81–Co2	107.1(2)	N91–Co1–O81	88.0(2)
N31–Co1–O21	92.5(2)	N72–Co1–N91	90.4(2)
O21–Co1–N91	88.0(2)	O21–Co1–N12	91.6(2)
O21–Co1–N72	88.4(2)	O21–Co1–O81	179.31(18)
O81–Co1–N12	88.0(2)	O81–Co1–N72	92.0(2)
N32–Co2–N11	88.8(2)	N32–Co2–O81	84.8(2)
N11–Co2–O81	84.9(2)	N52–Co2–N32	92.0(2)
N52–Co2–O61	89.9(2)	N52–Co2–O81	91.0(2)
N52–Co2–O41	90.7(2)	O41–Co2–N11	93.6(2)
O41–Co2–N32	90.3(2)	O61–Co2–N11	89.5(2)
O61–Co2–O41	87.76(17)	O81–Co2–O61	97.07(17)

As shown in Figure 1, the molecular structure of **1** consists of a highly asymmetric dinuclear unit with two cobalt(III) ions bridged by two pyrazolate groups and one phenoxide group with a Co···Co separation of 3.154 Å. This distance is slightly longer than those observed for other triply bridged dinuclear cobalt(III) complexes.[9] Most remarkably, the H_2phpz ligand shows four different coordination modes in the molecular structure of **1**: (i) quite unusual, the H_2phpz ligand remains neutral and is N-monodentate bound to Co2, with the ligand present in the 5-(2-hydroxyphenyl)-3-methylpyrazole mode; (ii) a uninegative $Hphpz^-$ ligand is NO-chelating to Co1; (iii) a second uninegative $Hphpz^-$ molecule acts as a NO-bidentate chelating ligand, and it links the two cobalt(III) ions through a phenoxido bridge; and (iv) two ligand molecules are doubly deprotonated, and these $phpz^{2-}$ ligands coordinate in a N_2O-tridentate manner to link the two cobalt(III) ions by a double pyrazolato bridge. In the last three modes the ligand is present in the 3-(2-hydroxyphenyl)-5-methylpyrazole conformation. As a result, both cobalt(III) ions have a distorted octahedral geometry and are in quite different coordination environments. The Co1 ion has a CoN_4O_2 donor set in a *trans* octahedral geometry, whilst the Co2 ion has a CoN_3O_3 donor set in a *mer* octahedral geometry. The cobalt(III) to oxygen and cobalt(III) to nitrogen bond lengths are in the ranges of 1.865–2.002 Å and 1.875–1.969 Å, respectively, as expected for low-spin cobalt(III) complexes.[10] The largest deviation from the octahedral geometry is observed for the *trans* angle which is O81–Co2–O41 174.90(17)°. The Co–O–Co angle is 107.09°, and it is slightly smaller than the angle normally observed for phenoxido-bridged dinuclear cobalt(III) complexes.[11,12] The least-squares plane of the aromatic ring of the N_2O-tridentate $phpz^{2-}$ ligand and the plane defined by Co1, Co2 and O81 have a dihedral angle of 38.11°. The bending angle of the bridging pyrazole least-squares planes to the Co1–N12–N11–Co2 and Co1–N31–N32–Co2 coordination planes is 5.36° and 5.64°, respectively. The dihedral angle between the planes of the two bridging pyrazole rings is 79.91°, whilst the dihedral angle between the $CoN_{pz}N_{pz}Co$ planes is 75.98°.

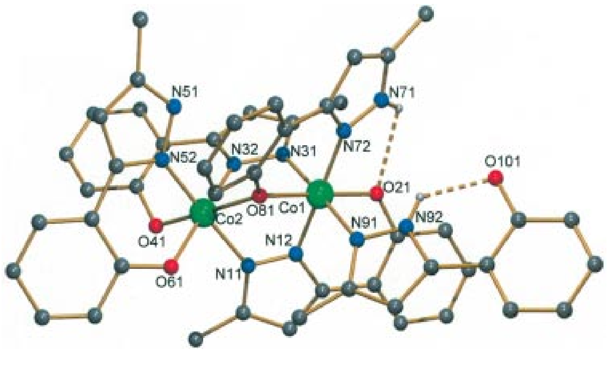

Figure 1. Pluton projection of the neutral complex $[Co_2(H_2phpz)(Hphpz)_2(phpz)_2]\cdot 3CH_3CN$ (**1**) showing the intramolecular hydrogen-bonding interactions. Hydrogen atoms that are not involved in hydrogen bonds and the acetonitrile molecules have been omitted for clarity.

The ligands adopt conformations that vary from nearly planar to considerably twisted with the dihedral angle between the phenyl and pyrazole ring planes ranging from 1.34° to 23.37°. These conformations are determined by the presence of strong intramolecular and intermolecular hydrogen bonds involving the O(phenol)–H and N(pz)–H moieties, as well as acetonitrile lattice molecules. The strongest intramolecular hydrogen bond involves the N–H group of the N-monodentate ligand bound to Co1 (N92–H92···O101 2.624 Å); the distance N71–H71···O21 of 2.756 Å would also suggest hydrogen bonding, but the angle of 107.9° is rather small. In addition, the O–H group of O101 participates in an intermolecular donor hydrogen-bonding interaction with a lattice acetonitrile molecule (O101–H101···N3 2.800 Å). The other two acetonitrile lattice molecules are at longer hydrogen-bond lengths (from N51 and N71). The acetonitrile molecules are kept rather weakly bound in the lattice, as is also seen from the elemental analyses (C, H and N), and some acetonitrile molecules might be replaced by atmospheric water. Table 2 gives some details of the hydrogen-bonding patterns.

Table 2. Hydrogen-bond details (distances [Å] and angles [°]) for $[Co_2(H_2phpz)(Hphpz)_2(phpz)_2]\cdot 3CH_3CN$ (**1**).

Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
N71–H71···O21	0.87	2.36	2.756(8)	107.9
N92–H92···O101	0.87	2.03	2.624(8)	124.6
O101–H101···N3	0.83	2.01	2.800(9)	159.8
N51–H51···N6	0.87	2.17	2.996(9)	157.9
N71–H71···N9	0.87	2.49	3.271(12)	149.8

Complexes **2** and **3** are isostructural, and they crystallize in the space group $P2_1/n$. In both cases, the asymmetric unit contains half of a centrosymmetric mononuclear unit. The metal ion has a *trans*-MN_2O_2 environment formed by two $Hphpz^-$ ligand molecules that bind in a NO-bidentate chelating manner in the 3-(2-hydroxyphenyl)-5-methylpyrazole mode. The molecular structure of **2** is shown in Figure 2. The structure of **3** is presented in the electronic supporting information. The coordination geometry of the NiN_2O_2 chromophore is slightly distorted square-planar [N1–Ni–O1 91.90°, O1–Ni–N1a 88.10(8)°]. The Ni–N [1.862(2) Å] and Ni–O1 [1.868(2) Å] bond lengths agree well with the values expected for a low-spin Ni^{II} ion in a square-planar environment.[13] The dihedral angle between the phenyl and pyrazole ring planes within the ligand is 4.62°. Examination of the crystallographic data (Supporting Information) reveals that the Cu^{II} coordination environment of complex **3** is somewhat more distorted than that of the Ni^{II} ion in **2**. As shown in Figure 2, there are two strong intramolecular hydrogen bonds with the acid N–H group as donor and the phenoxide group as acceptor [N2···O1a 2.612(3) Å, N2–H2···O1a 111°]. The crystal lattice is further stabilized by very weak π-π interactions involving the pyrazole rings; the shortest distance between the pyrazole planes is 3.919 Å. The closest Ni···Ni separation is 5.735 Å. Details for the Cu^{II} compound are given in the electronic supporting information.

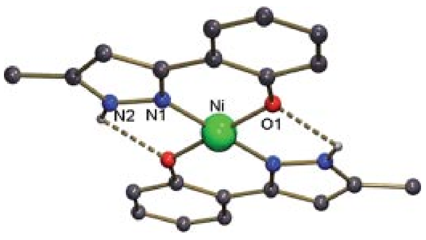

Figure 2. Pluton projection of the molecular structure of [Ni(Hphpz)$_2$] (**2**) showing the intramolecular hydrogen-bonding interactions. Hydrogen atoms that are not involved in hydrogen bonds have been omitted for clarity.

EPR and Magnetic Susceptibility

Complexes **1** and **2** display no EPR signal, neither in the solid state nor in CH_2Cl_2 solution, at room temperature or at 77 K. These results strongly indicate that **1** and **2** are diamagnetic ($S = 0$), as expected for low-spin d^6 octahedral Co^{III} complexes and low-spin d^8 square-planar Ni^{II} complexes.

The polycrystalline powder EPR spectrum of **3** recorded at room temperature and 77 K shows a broad spectrum ($g = 2.06$), and no resolved hyperfine splitting was observed (Figure 3). When Cu^{II} ions were separated by dilution as a 2% dopant in the diamagnetic host lattice of **2**, both hyperfine and superhyperfine splitting were observed (Figure 3). The superhyperfine structure is observed in the perpendicular region of the spectrum, arising from the interaction of the Cu^{II} unpaired electron with the two nitrogen donor atoms of two ligand molecules that results in a five line splitting ($A_N = 10$ G). The magnitude of $g_{\|}$ and $A_{\|}$ (2.25 and 200 G, respectively) and the five superhyperfine lines indicate that the Cu^{II} ion has an axial coordination geometry with two nitrogen donors in the equatorial plane,[14] in agreement with the X-ray crystal structure. The spectrum shows an unusual transition in the perpendicular region. This transition is caused by overshoot features which result in overlap of the perpendicular and the parallel transitions.[15]

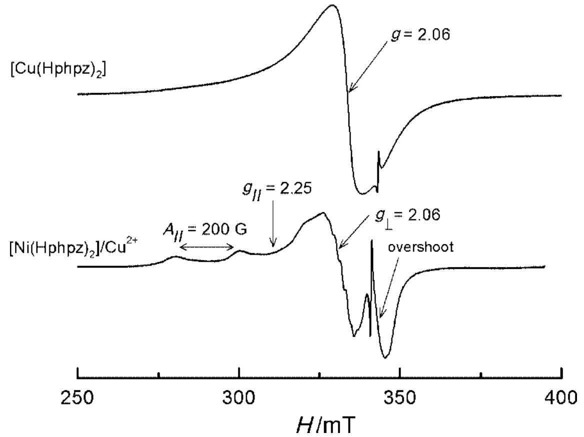

Figure 3. EPR spectra recorded at room temperature of [Cu(Hphpz)$_2$] (top) and [Ni(Hphpz)$_2$]/Cu^{2+} (bottom), with the radical DPPH marker at $g = 2.00$.

The temperature-dependent magnetic susceptibility of **3** in the range 2–300 K shows paramagnetic behaviour which results from the absence of effective exchange magnetic interactions between the mononuclear units. At 300 K, the $\chi_M T$ value is equal to 0.35 $cm^3\,K\,mol^{-1}$ which is close to the theoretical value of 0.375 $cm^3\,K\,mol^{-1}$ expected for a single noncoupled Cu^{II} centre ($S = 1/2$). The Ni compound was found to be diamagnetic.

Solution Chemistry

The positive-ion mass spectrum of **1** in methanol solution exhibits prominent signals at $m/z = 983$ and 810 that can be assigned to the molecular ion $\{[Co_2(H_2phpz)(Hphpz)_2(phpz)_2] + H\}^+$ and the fragment $\{[Co_2(Hphpz)_2(phpz)_2] + H\}^+$. These results suggest that complex **1** retains its dinuclear structure in solution. Therefore, the redox behaviour of **1** was studied in acetonitrile solution within the potential range –1.8 to 1.5 V vs. a Ag/AgCl electrode at ambient temperature (300 K). The cyclic voltammogram of complex **1** shows one irreversible wave at +1.2 V that could be assigned to the oxidation of the ligand on the electrode surface. No cathodic peak was observed, in agreement with the high stability of the dinuclear cobalt(III) core in solution.

The NMR spectroscopic analysis of **1** shows a complicated spectrum due to the low symmetry of the complex. The peaks could not be assigned because of the splitting of multiple peaks in the aromatic region of the complex as compared with the five peaks of the free ligand. Nevertheless, the integration of the aromatic peaks is in agreement with the different coordination modes of the ligand in the complex.

The study of the electrochemical behaviour of the Ni^{II} and Cu^{II} complexes was carried out in CH_2Cl_2 solution in the range +1.2 to –1 V. For both **2** and **3**, a quasireversible ligand oxidation at 0.9 V was observed in the positive range. No other redox processes were observed for **2**. For **3**, the additional anodic process observed at 0.62 V can be assigned to a quasireversible one-electron oxidation of Cu^{II} to Cu^{III}, and no cathodic process was observed. This result is not surprising given the preference of Cu^{I} for nonplanar coordination geometry and the anionic nature of the ligand.

Conclusions

In this study, the synthesis, crystal structure and spectroscopic characterization of an unusual dinuclear cobalt(III) complex and two new mononuclear Ni^{II} and Cu^{II} complexes have been presented. The reaction of the ligand 5(3)-(2-hydroxyphenyl)-3(5)-methylpyrazole with cobalt provided access to a new dinuclear complex, in which the versatility of the ligand showing four different coordination modes is beautifully illustrated. This dinuclear cobalt complex is unique, as it is triply bridged by two pyrazolate moieties and one phenoxide moiety with a Co···Co distance of 3.154 Å. This compound is stabilized through N–H···O intramolecular hydrogen interactions. Also, N–H···N intermolecular hydrogen interactions are present with acetonitrile lattice molecules. ESI-MS and cyclic voltammetry studies showed that the dinuclear complex is highly stable in solution. Additionally, the reaction of the ligand with Ni^{II} and Cu^{II} ions readily afforded mononuclear species of type $[M(Hphpz)_2]$, in which the ligand appears to be strong enough to generate the low-spin Ni^{II} cation. The EPR spectrum of the Cu^{II} dopant in this lattice confirmed the geometry and chromophore. Further work aimed at the synthesis of higher nuclearity species is in progress.

Experimental Section

General Remarks, Analysis and Spectroscopy: Starting materials were purchased from Aldrich, and all manipulations were performed using materials as received. The H_2phpz ligand was synthesized according to the reported procedure.[16] Elemental analyses (C, H and N) were performed with a Perkin–Elmer 2400 series II analyser. Infrared spectra (4000–300 cm^{-1}) were recorded with a Perkin–Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device, using the reflectance technique. Ligand field spectra were obtained with a Perkin–Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. The electrochemical measurements were performed with an Autolab PGstat10 potentiostat controlled by GPES4 software. A three-electrode system was used, consisting of a platinum working electrode, a platinum auxiliary electrode and a Ag/AgCl reference electrode. The experiments were carried out at room temp. under argon with tetrabutylammonium hexafluorophosphate as supporting electrolyte. All potentials are reported relative to Ag/AgCl. Electrospray mass spectra in acetonitrile/water (80:20) were recorded with a Thermo Finnigan AQA apparatus. X-band powder EPR spectra were obtained with a JEOL RE2x electron-spin resonance spectrometer using DPPH (g = 2.0036) as a standard. Magnetic susceptibility measurements (2–300 K) were carried out at 0.1 T using a Quantum Design MPMS-5 5 T SQUID magnetometer.

Synthesis of $[Co_2(H_2phpz)(Hphpz)_2(phpz)_2]\cdot 3CH_3CN$ (1): A solution of 5(3)-(2-hydroxyphenyl)-3(5)-methylpyrazole (61 mg, 0.35 mmol) and triethylamine (67 mg, 0.66 mmol) in acetonitrile (7 mL) was slowly added to a solution of $Co(ClO_4)_2\cdot 6H_2O$ (66 mg, 0.18 mmol) in acetonitrile (2 mL). The resulting purple solution was stirred for 5 min to give a purple precipitate. The purple solid was collected by filtration, washed with acetonitrile and ether and dried in air. Yield: 26.03 mg (34%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of the filtrate. $C_{56}H_{53}Co_2N_{13}O_5$ (1105.97): calcd. C 60.82, H 4.83, N 16.46; found C 58.13, H 5.00, N 15.08. Loss of some lattice acetonitrile molecules may result in lower C, H and N analyses as the acetonitrile molecules are weakly held in the lattice; replacement of one acetonitrile molecule by three molecules of water would generate a more accurate C,H,N analysis [complex·$2CH_3CN\cdot 3H_2O$, $C_{54}H_{56}Co_2N_{12}O_8$ (1118.98): calcd. C 57.96, H 5.04, N 15.02]. IR: $\tilde{\nu}$ = 3425 (w), 3280 (w), 1596 (m), 1558 (s), 1463 (s), 1456 (s), 1299 (m), 1229 (s), 1188 (w), 1116 (m), 1038 (w), 986 (s), 850 (s), 772 (m), 752 (m), 744 (m), 641 (m), 602 (m), 584 (s), 436 (m), 418 (s) cm^{-1}. UV/Vis: λ_{max} = 576, 335, 271 nm.

Synthesis of $[Ni(Hphpz)_2]$ (2): The ligand H_2phpz (161 mg, 0.92 mmol) and 1 M methanol solution of Bu_4NOH (2 mL, 2 mmol) were dissolved in methanol (10 mL). To this solution was added a solution of $Ni(ClO_4)_2\cdot 6H_2O$ (367 mg, 1 mmol) in methanol (10 mL), and the mixture was then stirred. A green microcrystalline precipitate formed immediately. After a few minutes, the solid (230 mg) was collected by filtration and dissolved in CH_2Cl_2 (20 mL). The dark-green solution was layered with Et_2O in various sealed tubes. After a few days, large dark-green crystals suitable for X-ray crystallography were collected. Yield: 27.53 mg (15%). $C_{20}H_{18}NiN_4O_2$ (405.09): calcd. C 53.16, H 4.19, N 11.95 (The calculated values given here are for the complex **2**·$0.75CH_2Cl_2$. The presence of CH_2Cl_2 is not unexpected as the complex was crystallized from this solvent); found C 53.87, H 4.36, N 12.42. IR: $\tilde{\nu}$ = 3299 (s), 1600 (s), 1553 (s), 1471 (s), 1412 (s), 1314 (s), 1249 (s), 1197 (m), 1121 (m), 1039 (m), 1117 (m), 864 (s), 788 (s), 738 (m), 668 (m), 645 (m), 587 (s), 475 (m), 384 (s) cm^{-1}. UV/Vis: λ_{max} =

Table 3. Crystal data and structure refinements for $[Co_2(H_2phpz)(Hphpz)_2(phpz)_2]\cdot 3CH_3CN$ (**1**), $[Ni(Hphpz)_2]$ (**2**) and $[Cu(Hphpz)_2]$ (**3**).

Formula	$C_{56}H_{53}Co_2N_{13}O_5$ (**1**)	$C_{20}H_{18}NiN_4O_2$ (**2**)	$C_{20}H_{18}CuN_4O_2$ (**3**)
Formula mass [g mol^{-1}]	1105.97	405.09	409.93
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a [Å]	10.6796(14)	12.637(8)	12.5018(13)
b [Å]	26.103(3)	5.735(3)	5.6636(6)
c [Å]	18.3933(12)	12.736(4)	12.785(4)
β [°]	92.492(8)	110.64(2)	110.420(11)
V [Å^3]	5122.6(10)	863.8(8)	848.4(3)
Z	4	2	2
$D_{calcd.}$ [g cm^{-3}]	1.434	1.557	1.605
Crystal size [mm]	0.22 × 0.12 × 0.04	0.11 × 0.13 × 0.18	0.38 × 0.07 × 0.04
Crystal shape and colour	dark-brown, regular platelets	green needles	dark brown-red needles
Number of collected reflections (unique)	76586 (9012)	6786 (2121)	9188 (1494)
Number of observed reflections [$I_o > 2\sigma(I_o)$]	6636	1883	1089
Internal R factor	0.0953	0.058	0.052
Number of parameters	694	124	125
Goodness-of-fit S on F^2	1.247	1.11	1.08
μ [mm^{-1}]	0.712	1.147	1.312
R_1[a] [$I > 2\sigma(I)$]	0.0861	0.0547	0.0458
wR_2[b] (all data)	0.1780	0.1495	0.0870
T [K]	208	293	208

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

622, 490, 415, 360, 268 nm. The reaction of 2 equiv. H_2phpz with 1 equiv. $Ni(OAc)_2$ in acetonitrile and in the absence of base afforded **2** as a polycrystalline sample with a yield of 76%. The Cu^{II}-doped Ni^{II} compound was prepared using this method but using a Ni/Cu ratio of 100:2.

Synthesis of [Cu(Hphpz)$_2$] (3): A solution of H_2phpz (35 mg, 0.20 mmol) and sodium methoxide (22 mg, 0.40 mmol) in methanol (5 mL) was slowly added to a solution of $Cu(ClO_4)_2·6H_2O$ (76 mg, 0.20 mmol) in methanol (2 mL). The resulting green solution was stirred for 5 min to give a green precipitate. The solid was removed by filtration, and slow evaporation of the filtrate gave large dark-brown-red needles suitable for X-ray crystallography. Yield: 23.78 mg (58%). $C_{20}H_{18}CuN_4O_2$ (409.93): calcd. C 58.60, H 4.43, N 13.67; found C 58.43, H 4.30, N 13.76. IR: $\tilde{\nu}$ = 3311 (s), 1599 (m), 1548 (s), 1464 (s), 1316 (s), 1247 (m), 1196 (w), 1121 (m), 1065 (m), 1039 (w), 1018 (m), 857 (s), 791 (m), 739 (m), 668 (m), 641 (m), 618 (m), 593 (s), 575 (s), 470 (m), 371 (s) cm^{-1}. UV/Vis: λ_{max} = 660, 455, 380, 350, 263 nm. The reaction of 2 equiv. H_2phpz with 1 equiv. $Cu(OAc)_2$ in acetonitrile and in the absence of base afforded **3** as a polycrystalline sample with a yield of 72%.

X-ray Crystallographic Study: Intensity data for single crystals were collected using Mo-K_α radiation (λ = 0.71073 Å) with a Nonius KappaCCD diffractometer. Crystal and refinement data are shown in Table 3 for **1**, **2** and **3**. The intensity data were corrected for Lorentz and polarization effects, and for absorption (multiscan absorption correction[17]). The structures were solved by Patterson methods.[18] The programs EvalCCD, DIRDIF96 and SHELXL-97 were used for data reduction, structure solution, refinement and evaluation.[19–22] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed at calculated positions and were refined riding on the parent atoms. Geometric calculations and molecular graphics were performed with the PLATON package.[23]

CCDC-628568, -639396 and -641268 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Table S1 summarizes the selected bond lengths [Å] and angles [°] for the complexes [Ni(Hphpz)$_2$] (**2**) and [Cu(Hphpz)$_2$] (**3**), and Figure S1 shows the crystal structure of [Cu(Hphpz)$_2$] (**3**).

Acknowledgments

This work was financially supported by the Netherlands Economy, Ecology, Technology (EET) programme, the EC-RTN "QuEMolNa" (No. MRTN-CT-2003-504880) and the ECNetwork of Excellence "MAGMANet" (No. 515767-2). S. T. acknowledges the Netherlands Organization for Scientific Research (NWO) for a Veni grant. We would like to acknowledge Prof. L. J. de Jongh for useful discussions.

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Received: March 21, 2007