Structural and magnetic variability of cobalt(II) complexes with bridging pyrazolate ligands bearing appended imine groups[†]

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The synthesis of new binucleating pyrazole-derived ligands (HL², HL³) with bulky 2,6-diisopropylphenylimine side arms and backbone phenyl groups at the pyrazole-C⁴ and/or at the imine-C, which are derivatives from the known ligand HL¹, is reported. Crystallographic analyses of three cobalt(II) complexes coordinated by ligands $[L^{1-3}]^-$ reveal distinct metal to ligand ratios and different structural motifs in the solid state: $[L^1Co_2Cl_3(H_2O)_2(EtOH)]$ (1), $[(L^2)_3Co_4Cl_5]$ (2), or $[(L^3)_2Co_4Cl_6(H_2O)_5]$ (3). Metal ions are five-coordinate in 1, four- and six-coordinate in 2, and six-coordinate in 3. UV-Vis spectroscopy and ESI mass spectrometry suggest that complexes 2 and 3 retain their structures also in solution, whereas 1 partially dimerizes and is in equilibrium with tetrametallic species akin to 3. Magnetic susceptibility measurements indicate weak to moderate antiferromagnetic coupling between five-coordinate or between six-coordinate cobalt(II) ions, but weak ferromagnetic coupling between four- and six-coordinate cobalt(II).

Introduction

Bi- and oligonuclear complexes are attracting a lot of attention, mainly because of the general interest in cooperative effects that may occur for, inter alia, synergetic reactivity towards small substrates or magnetic properties.^{1,2} Compartmental ligand systems are of pivotal importance in this context, since they allow to position two or more metal ions in proper spatial location, and in the presence of suitable coligands they may even support the controlled aggregation giving high-nuclearity complexes. Hence the design of elaborate multidentate ligand systems and the investigation of their fundamental coordination chemistry is a cornerstone on the way to achieving and understanding multimetal cooperativity.³⁻⁵ Binucleating ligands can be classified by their central bridging groups. The negatively charged pyrazolate is well established as a popular bridging unit that may span two metal ions at favorable distances of around 3.0-4.5 Å.^{6,7} Further control of the metal-metal separation as well as of the individual metal ion coordination spheres can be realized by introducing chelate side arms in the 3- and 5-positions of the pyrazolate heterocycle, and metal complexes of compartmental pyrazolate-based ligands have shown great potential in, e.g., metallobiosite modelling, molecular magnetism, and two-center organometallic catalysis.8-12

A particular subclass of such pyrazolate ligand scaffolds features appended imine functions with bulky aryl substituents.¹³⁻¹⁵ These ligands can be viewed as binucleating versions of the intensively studied α -diimine type ligands. Their palladium(II) and nickel(II) complexes (after activation with MAO) are efficient catalysts for olefin poylmerization and they feature an interesting organometallic chemistry, with unique effects arising from cooperativity of the proximate metal ions.¹⁵ More recently, such ligands also gave rise to some bimetallic platinum and heterobimetallic platinum/copper chemistry.¹⁶ While palladium(II) chloride complexes of the binucleating pyrazole/imine ligands are square-planar (**A**, Scheme 1), the corresponding nickel(II) chloride or bromide complexes tend to form oligonuclear aggregates $[LNi_2X_3]_a$ (n = 2,3) with five- or six-coordinate high-spin metal ions.^{13,15} These aggregates may give rise to more open structures $[LNi_2X_3(solv)_x]_a$ in the presence of coordinating solvents (*e.g.*, **B**, Scheme 1).



Scheme 1 Different multinuclear pyrazole/imine complexes.

With copper(II) acetate, two ligands were found to encapsulate an unusual edge-sharing bitetrahedral Cu_6O_2 core.¹⁷ In order further elaborate the chemistry of this ligand class and to probe the influence of substituents either at the outer N-bound aryl groups or the ligand backbone, we have recently developed synthetic routes to new functionalized pyrazole building blocks that now provide access to a greater variety of ligand derivatives.¹⁸ Two new

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pyrazole/imine binucleating ligands HL^2 and HL^3 with backbone phenyl groups are reported here. Structures as well as spectral and magnetic properties of a series of cobalt(II) complexes are described, using a set of three ligands with different backbone substitution pattern (including the two new ligands). The d⁷ cobalt(II) ion was chosen because of its very flexible coordination behavior, which was expected to provide some clues about the coordination landscape of this particular class of pyrazole-derived ligands.

Results and discussion

Synthesis and structural characterization of the ligands

Type **C** pyrazole building blocks have been prepared according to the recently reported methods.¹⁸ Following the procedure for the known HL^1 ($R^2 = Me$), acid-catalyzed condensation of the respective dicarbonyl compounds with 2,6-diisopropylaniline in refluxing toluene yields the new ligands HL^2 and HL^3 that bear one or three phenyl substituents at the backbone ($R^2 = Ph$; Scheme 2).



Scheme 2 Ligand synthesis.

 HL^2 and HL^3 were isolated as white (HL^2) and yellow (HL^3) solids in yields up to 94%. Both new ligands have been fully characterized by ${}^{1}H/{}^{13}C$ NMR and IR spectroscopy, mass spectrometry (high resolution/EI) and elemental analysis. Single crystals of ligand HL^2 suitable for X-ray diffraction analysis were grown by recrystallization from ethanol. Single crystals of HL^3 were obtained from acetone/hexane, but unfortunately they were poorly diffracting. While the X-ray data clearly reveal the constitution and the crystal packing, we refrain from discussing metric parameters of HL^3 .

The molecular structures of HL² and HL³ are shown in Fig. 1 and Fig. S1.[†] The iminometyl groups, which are attached to the 3- and 5-positions are coplanar with the pyrazole ring. In both cases the two side arms are orientated in anti-conformation: while the N(3) is located close to the pyrazole N(1), the N(4) side arm is directed towards the backside pointing away from pyrazole-N(2). Hydrogen bonding between the pyrazole-N(1)-H and the side-arm N(3') atoms of a neighboring molecule results in a dimeric structure for HL², while no such dimerization but hydrogen bonding to an undefined solvent molecule is observed in the case HL³. The hydrogen bonding motif in HL² that involves the substituent in the pyrazole-5 position is quite unusual, since most N-unsubstituted pyrazoles give supramolecular arrangements where only the pyrazole-N and -NH are involved in intermolecular hydrogen bonding (dimers, trimers, tetramers, hexamers or catemers).18,19



Fig. 1 View of the hydrogen bond structure of HL^2 (50% probability ellipsoids). In the interest of clarity the side arm aryl groups and most of the hydrogen atoms have been omitted. Selected atom distances (Å) and angles (°): N(1)…N(3') 2.923(2), N1-N2 1.340(2), N(1)-H(1)-N(3') 166.17(2).

Synthesis and structural characterisation of Co(II) complexes

For the synthesis of cobalt(II) complexes the respective ligand (HL^1-HL^3) was deprotonated with 1 equiv. of KO'Bu in THF. Subsequent addition of 2 equiv. of anhydrous CoCl₂ resulted in the formation of deep-green solutions. Complexes **1–3** were finally isolated in good yields after crystallization (see Experimental). Distinct molecular structures were found for the three different ligands.

Purple crystals of $[L^1Co_2Cl_3(H_2O)_2(EtOH)]$ (1) were grown by slow evaporation of a solution of the crude complex in CHCl₃/EtOH. The molecular structure of 1 is depicted in Fig. 2.

1 is a binuclear complex with $[L^1]^-$ acting as a bis(bidentate) ligand, as anticipated. Both metal ions are found in distorted trigonal bipyramidal coordination environment ($\tau = 0.92$ for Co(1) and 0.68 for Co(2)).²⁰ Co(1) is additionally ligated by one chloride and two H2O molecules, while two chlorides and an EtOH solvent molecule are bound to Co(2). Within the bimetallic pocket the two H₂O molecules at Co(1) and the two chloride ligands at Co(2) are linked via two intramolecular O-H...Cl hydrogen bonds with $d(O(1)\cdots Cl(3)) = 3.12$ Å and $d(O(2)\cdots Cl(2)) =$ 3.07 Å (Fig. 2). Various hydrogen bonding motifs between metalbound water and chloride ligands have also been observed in a series of related nickel(II) complexes,²¹ and several examples of a single O-H...X hydrogen bond within the bimetallic pocket of pyrazolate-based bimetallic complexes are known,²² but the arrangement in 1 with double intramolecular $O-H \cdots X$ bridges represents a novel pattern. Co-Cl distances (2.33-2.35 Å) and Co-O bond lenghts (2.01–2.09 Å) in 1 are in the expected ranges^{23,24} and Co-Cl bonds are not very different from those in some pyrazolatebased dicobalt(II) complexes with N-H····Cl hydrogen bonds involving side arm donors of the binucleating ligand scaffold.25,26 Interestingly, an extensive hydrogen bonding network involving the chlorido, water and ethanol ligands leads to dimeric aggregates



Fig. 2 Left: molecular structure of 1 (50% probability ellipsoids). In the interest of clarity most hydrogen atoms except those of the OH groups of water and EtOH ligands have been omitted. Selected atom distances (Å): Co(1)-N(1) 2.113(2), Co(1)-N(3) 2.077(2), Co(1)-O(1) 2.017(2), Co(1)-O(2) 2.038(2), Co(1)-Cl(1) 2.3315(7), Co(2)-N(2) 2.0947(19), Co(2)-N(4) 2.074(2), Co(2)-O(3) 2.0991(18), Co(2)-Cl(2) 2.3482(6), Co(2)-Cl(3) 2.3304(7), Co(1) \cdots Co(2) 4.4191(5). Right: view of the hydrogen bonding in dimeric aggregates of 1.



Fig. 3 Left: molecular structure of 2 (50% probability ellipsoids). In the interest of clarity all hydrogen atoms and 2,6-diisopropylphenyl rings have been omitted. Selected atom distances (Å): Co(1)-N(1) 2.016(3), Co(1)-N(3) 2.089(3), Co(1)-Cl(1) 2.2831(9), Co(1)-Cl(4) 2.1958(10), Co(2)-N(2) 2.044(3), Co(2)-N(4) 2.190(3), Co(2)-N(21) 2.031(3), Co(2)-N(23) 2.412(3), Co(2)-Cl(2) 2.4877(9), Co(2)-Cl(3) 2.4288(9), Co(3)-N(11) 2.015(3), Co(3)-N(13) 2.089(3), Co(3)-Cl(3) 2.2765(10), Co(3)-Cl(5) 2.1857(12), Co(4)-N(12) 2.053(3), Co(4)-N(14) 2.209(3), Co(4)-N(22) 2.032(3), Co(4)-N(24) 2.4547(3), Co(4)-Cl(1) 2.4182(9), Co(4)-Cl(2) 2.4437(10), Co(1) \cdots Co(2) 4.2348(6), Co(1) \cdots Co(3) 6.6501(7), Co(1) \cdots Co(4) 3.7711(6), Co(2) \cdots Co(3) 3.8068(7), Co(2) \cdots Co(4) 3.9522(7), Co(3) \cdots Co(4) 4.2490(7). Right: view of the tetranuclear metal core of **2**.

of two roughly perpendicular molecules **1** in the solid state (Fig. 2, right).

The solid state structure of $[(L^2)_3Co_4Cl_5]$ (2) consists of four metal ions and three ligands $[L^2]^-$ (Fig. 3). Co(2) and Co(4) have strongly distorted octahedral coordination spheres and are doubly bridged by a pyrazolate ligand and a chloride. In contrast, Co(1) and Co(3) are only four-coordinate with distorted tetrahedral environment. They are each singly connected to the central Co(2)/Co(4) pair *via* a pyrazolato bridge to one of the central metal atoms and *via* a bridging chloride to the other. The appearance of two different metal coordination geometries (octahedral and tetrahedral) in one compound is relatively rare.²⁶⁻²⁹ A view of the central core of **2** (showing only the metal ions with their surrounding atoms) is presented in Fig. 3, right. The lengths of the terminal Co-Cl bonds (~2.2 Å) are in the common range for tetrahedrally coordinated cobalt(II) ions.³⁰ Distances of the bridging Cl atoms from the tetrahedral Co(1) and Co(3) ions (~2.3 Å) and from the octahedral Co(2) and Co(4) ions (~2.5 Å) differ significantly. In general, all metal–ligand bonds are longer for the six-coordinate cobalt(II) ions than for the four-coordinate cobalt(II) ions, as expected.

Complex 3, prepared from $CoCl_2$ and $[L^3]^-$, forms a tetranuclear array $[(L^3)_2Co_4Cl_6(H_2O)_5]$ that is composed of two bimetallic $\{L^3Co_2Cl_3\}$ building blocks (Fig. 4). All metal ions are found in disordered octahedral coordination sphere. The $Co(1) \cdots Co(2)$ distance spanned by the pyrazolate is ~4.0 Å, while the distance



Fig. 4 Molecular structure of 3 (50% probability ellipsoids). In the interest of clarity all hydrogen atoms have been omitted. Selected atom distances (Å): Co(1)-N(1) 2.024(3), Co(1)-N(3) 2.161(3), Co(1)-O(1) 2.175(4), Co(1)-O(2) 2.103(13), Co(1)-Cl(4') 2.3752(11), Co(1)-Cl(5) 2.6949(5), Co(2)-N(2) 2.016(3), Co(2)-N(4) 2.169(3), Co(2)-O(3) 1.993(8), Co(2)-Cl(3) 2.529(5), Co(2)-Cl(4) 2.3576(11), Co(2)-Cl(5) 2.6599(6), Co(1)-Co(2) 4.0370(7), Co(1)-Co(2') 3.5182(9), Co(1)-Co(1') 5.3898(11).

 $Co(1) \cdots Co(2')$ between the two subunits is shorter at ~3.5 Å. The two subunits are connected by two chloride bridges that span the shorter edges of the flat tetrametallic array, and by a unique μ_4 -Cl atom that is nested at the center of the complex. The Co-Cl distances towards this μ_4 -chloride are quite long at 2.53 to 2.69 Å. μ_4 -Cl atoms are rare,³¹ and most of the known examples are found in late transition metal chemistry (copper, silver and mercury).³² In the nickel(II) case the present type of pyrazole/imine binucleating ligands gave complexes [LNi₂X₃]₃ (X = Cl, Br) with a unique μ_6 halide in the center of the hexametallic cage. These cages open up in the presence of coordinating solvents to yield $Ni_4(\mu_4-X)$ species akin to 3.^{13,15} 3 appears to be the first example of a μ_4 chlorido ligand in cobalt cooodination chemistry. All remaining coordination sites above and below the central $Co_4(\mu_4$ -Cl) plane in 3 are statistically occupied by metal bound water molecules and additional chlorido ligands.

Stability of the complexes in solution

UV-Vis spectra of all complexes have been collected in CH_2Cl_2 and in the solid state (diffuse reflectance) in order to elucidate whether the oligonuclear species found in the crystalline material are also present in solution (Table 1, Fig. S2†). Absorption maxima for **2** and **3** are quite similar when measured in CH_2Cl_2 or in the solid state, suggesting that the tetranuclear complexes stay essentially intact upon dissolving the crystalline material. In contrast, spectra for **1** differ significantly when measured in CH_2Cl_2 or in the solid state, with the absorption maxima in solution closely resembling those of the tetranuclear complex **3**. One may thus assume that the complex $[L^1Co_2Cl_3(H_2O)_2(EtOH)]$ (**1**) with its labile (H)O-H… Cl bridges undergoes dimerization and partly transforms to

	1	2	3
Solution	531(85)		
	556(101)	580(237)	561(271)
	587(113)	635(226)	584(307)
	672(111)	688(331)	671(305)
Solid state	533		
	583	579	562
	628	633	584
	659	688	673

its tetrametallic analogue $[(L^1)_2Co_4Cl_6(solvent)_5]$ (1') in solution. One should note that species 1' and the dimeric aggregates of 1 found in the solid state with composition $[\{L^1Co_2Cl_3(solvent)_3\}_2]$ (see Fig. 2, right) differ by a single solvent molecule only. Thus it is well conceivable that two molecules of 1 are in solvent-dependent equilibrium with tetranuclear species 1' akin to 3.

This is further corroborated by the ESI⁺ mass spectrum of a MeCN solution of 1 (Fig. 5), which shows major peaks not only at m/z 671 (corresponding to $[L^1Co_2Cl_2]^+$), but also at m/z 1119 and 1379, characteristic for the ions $[(L^1)_2Co_2Cl]^+$ and $[(L^1)_2Co_4Cl_5]^+$.



Fig. 5 Positive ion ESI-MS spectrum for 1 in MeCN solution; the inset shows the observed and calculated HR-MS isotopic distribution for the peak at m/z 671 corresponding to [L¹Co₂Cl₂]^{*}.

Magnetic properties

Magnetic susceptibilities for powdered samples of singlecrystalline material of complexes **1–3** were measured in a magnetic field of 0.5 T in the temperature range 295–2 K (Fig. 6). Magnetic data analyses of cobalt(II) complexes are often complicated by the strong anisotropy of this particular ion, which may preclude a simple spin-only simulation approach.³³ However, using more sophisticated models often bears a considerable risk of overparameterization, and hence a treatment through the spin-only formalism is advisable as a first approximation. One should keep in mind though that the determination of magnetic parameters from simulation of the susceptibility data for polycrystalline powder material using such simplified models has to be regarded with caution.

The μ_{eff} value at 295 K for 1 (6.36 μ_{B}) is higher than the spin-only value for two S = 3/2 ions (5.48 μ_{B} for g = 2.0) but



Fig. 6 μ_{eff} vs. *T* plot for **1** (circles), **2** (triangles) and **3** (squares). The solid lines represent the calculated curve fits (see text).

not unexpected in view of the common g values for cobalt(II) (expected 6.13 $\mu_{\rm B}$ for g = 2.24). Upon lowering the temperature $\mu_{\rm eff}$ drops more and more rapidly to finally reach 1.95 $\mu_{\rm B}$ at 2 K, suggesting antiferromagnetic coupling and an S = 0 ground state. The experimental data for 1 were modelled by using a fitting procedure to the appropriate Heisenberg-Dirac-van-Vleck (HDvV) spin Hamiltonian for isotropic exchange coupling and Zeeman splitting, eqn (1).³⁴

$$\hat{H} = -J\hat{S}_1\hat{S}_2 + g\mu_{\rm B}B(\hat{S}_1 + \hat{S}_2) \tag{1}$$

A Curie-behaved paramagnetic impurity (PI) with spin S =3/2 and temperature-independent paramagnetism (TIP) were included according to $\chi_{calc} = (1 - PI)\cdot\chi + PI\cdot\chi_{mono} + TIP.^{35}$ Note, that some single-ion anisotropy should be present in view of the unsymmetrical surroundings of the cobalt ions, which are severely distorted from a perfect octahedron. However, due to the antiferromagnetic coupling that gives an S = 0 ground state anisotropies will have no effect in the low temperature regime, while the effect at higher temperatures is relatively small anyway. A good quality fit is thus obtained in the simple Heisenberg model. Best fit parameters for 1 are g = 2.24, J = -1.7 cm⁻¹, PI = 2.5%(fixed)³⁶ and $TIP = 19.0 \times 10^{-4} \text{ cm}^3 \text{mol}^{-1}$. If a zero field splitting (ZFS) parameter D was included into the fitting procedure for 1, D converged to zero during data simulation, in agreement with the overall S = 0 ground state. Since the local axial ZFS of five-coordinated cobalt(II) can be very large,³⁷ in an alternative simulation the coupling parameter J was fixed to zero and only a D parameter used to describe the low temperature magnetic behaviour, but no reasonable fit could be obtained in this case (see Fig. S3[†]).

Magnetic measurements for **2** show the presence of antiferromagnetic interactions, as indicated by the decrease of the magnetic moment from 9.64 $\mu_{\rm B}$ (295 K) to 4.41 $\mu_{\rm B}$ (2 K). In view of the structural features, the magnetic model for **2** is based on a central antiferromagnetically coupled dimer of six-coordinate cobalt(II) ions (Co(2) and Co(4) with coupling constant J_1), with two appended four-coordinate cobalt(II) ions as wingtips (Co(1) and Co(3)). Fig. 7 (left) illustrates the possible interaction pathways in **2**.

The appropriate Heisenberg-Dirac-van-Vleck (HDvV) spin Hamiltonian includes three isotropic exchange coupling terms, Zeeman splitting and zero field splitting, eqn (2).



Fig. 7 Coupling schemes for 2 (left) and 3 (right).

$$\hat{H} - 2J_1 \hat{S}_2 \hat{S}_4 - 2J_2 (\hat{S}_1 \hat{S}_2 + \hat{S}_3 \hat{S}_4) - 2J_3 (\hat{S}_1 \hat{S}_4 + \hat{S}_2 \hat{S}_3) + g\mu_{\rm B} B \sum_{i=1}^4 \hat{S}_{zi} + \sum_{i=1,3} D_i [S_{zi}^2 - 1/3S_i (S_i + 1)]$$
⁽²⁾

Best fit parameters are $g_1 = g_3 = 2.33$, $g_2 = g_4 = 2.60$, $J_1 =$ -4.6 cm^{-1} , $J_2 = +0.4 \text{ cm}^{-1}$, $J_3 = +0.003 \text{ cm}^{-1}$, PI = 5.0% (fixed) and $TIP = 33.5 \times 10^{-4} \text{ cm}^3 \text{mol}^{-1}$ (fixed). ZFS parameters are $|D_1| = |D_3| = 11.5$ cm⁻¹; to reduce the number of parameters $|D_2|$ and $|D_4|$ for the central pair of six-coordinate cobalt(II) ions were fixed to zero because of the antiferromagnetic coupling between them, which is also reflected by the relatively large negative value for J_1 that results from the double pyrazolate and chloride bridging. g values much larger than 2.0 are common for octahedral high-spin cobalt(II), because of the strong first order orbital momentum contribution to the spin ground state.³⁸ Due to the symmetry of the Hamiltonian, assignment of J_2 and J_3 is tentative; furthermore, one of these two positive coupling constants (J_3) is very small and can be taken as zero. The positive value of the remaining J_2 for the coupling between octahedral and the tetrahedral cobalt(II) ions, *i.e.*, between the central hinge and the wingtips of the tetrametallic core, may be explained in terms of a partial orthogonality situation of the magnetic orbitals.³⁴ These are e_g and t_{2g} for octahedral and t_2 for tetrahedral cobalt(II) high spin ions. Weak ferromagnetic coupling was also observed in a chain of alternating octahedral and tetrahedral cobalt(II) sites.³⁹ It should be noted, however, that the magnetic properties of 2 can be described equally well using a simple dimer model for the central dicopper(II) core with two additional Curie-behaved terms for isolated tetrahedral cobalt(II) ions with zero field splitting. In this case the decrease of $\mu_{\rm eff}$ is associated with a somewhat smaller J_1 (-3.8 cm⁻¹). In view of the possible over-parameterization when applying the complete model for 2 (Fig. 7, left), the 3D error surfaces for the pairs J_1 - J_2 and J_2 - J_3 were calculated (Fig. S4[†]). For the pair $J_2 - J_3$ only one distinct minimum can be observed, indicating that these two parameters are independent. Two minima are observed for the J_1 - J_2 pair, which reflects the two different models (the model sketched in the left part of Fig. 7 and the dimer model with $J_2 = 0$; see Fig. S4[†]).

According to the molecular structure of **3**, three interaction pathways exist also in this case (Fig. 7, right). The appropriate Heisenberg-Dirac-van-Vleck (HDvV) spin Hamiltonian includes three isotropic exchange coupling constants and Zeeman splitting, eqn (3).

$$\begin{aligned} \hat{H} &= -2J_{1}(\hat{S}_{1}\hat{S}_{3} + \hat{S}_{2}\hat{S}_{4}) - 2J_{2}(\hat{S}_{1}\hat{S}_{2} + \hat{S}_{3}\hat{S}_{4}) - 2J_{3}(\hat{S}_{1}\hat{S}_{4} + \hat{S}_{2}\hat{S}_{3}) \\ &+ g\mu_{B}B\sum_{i=1}^{4}\hat{S}_{zi} \end{aligned}$$
(3)

Even though all three coupling constants should be intuitively different, the best fit result was obtained for

	HL ²	[L ¹ Co ₂ Cl ₃ (H ₂ O) ₂ (EtOH)]· 1.5CHCl ₃ (1)	[(L ²) ₃ Co ₄ Cl ₅]·0.5 (THF)·MeCN (2)	[(L ³) ₂ Co ₄ Cl ₆ (H ₂ O) ₅]·2CHCl ₃ (3)
Empirical formula	$C_{35}H_{42}N_4$	C35.5H54.5Cl7.5Co2N4O3	$C_{109}H_{130}Cl_5Co_4N_{13}O_{0.5}$	$C_{96}H_{100}Cl_{12}Co_4N_8O_5$
Formula weight	518.73	969.07	2043.23	2106.96
Crystal size/mm	$0.33 \times 0.23 \times 0.19$	$0.53 \times 0.27 \times 0.22$	$0.56 \times 0.39 \times 0.26$	$0.24 \times 0.18 \times 0.12$
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i> (No. 15)	<i>Iba</i> 2 (No. 45)	$P2_1/n$ (No. 14)	<i>P</i> -1 (No. 2)
a/Å	27.7190(14)	16.3211(11)	16.5141(4)	11.2650(7)
b/Å	8.8990(3)	17.7522(11)	22.4226(4)	15.1857(9)
c/Å	25.4394(14)	31.585(3)	31.4461(9)	17.6502(10)
$\alpha /^{\circ}$	90	90	90	112.618(4)
$\beta/^{\circ}$	100.727(4)	90	102.388(2)	90.388(5)
$\gamma/^{\circ}$	90	90	90	106.495(4)
$V/Å^3$	6165.5(5)	9151.2(11)	11373.0(5)	2649.4
Z	8	8	4	1
$ ho_{ m calcd.}/ m g~cm^{-3}$	1.118	1.407	1.193	1.321
F(000)	2240	4008	4288	1084
μ/mm^{-1}	0.066	1.200	0.740	0.969
hkl range	± 34 , -11 to ± 10 , ± 32	$\pm 20, \pm 22, \pm 39$	$\pm 20, -27 \text{ to } +25, \pm 38$	$\pm 14, \pm 19, -22$ to ± 20
θ range/°	1.50 to 26.78	1.69 to 26.58	1.12 to 25.74	1.90 to 27.03
Measured refl.	26988	37227	86436	22714
Unique refl./ R_{int}	6546 [0.1088]	9530 [0.0387]	21492 [0.1459]	11412 [0.0392]
Observed refl. $(I > 2\sigma(I))$	4224	9162	16904	8282
Ref. param./restraints	356/0	519/4	1210/0	587/0
Goodness-of-fit	0.999	1.049	1.028	1.041
$R1$, w $R2$ ($I > 2\sigma(I)$)	0.0617, 0.1224	0.0298, 0.0754	0.0677, 0.1914	0.0688, 0.1654
R1, w $R2$ (all data)	0.1073, 0.1383	0.0314, 0.0761	0.0827, 0.2050	0.0974, 0.1775
Resid. el. dens./e Å ⁻³	0.212/-0.238	0.582/-0.615	1.488/-1.196	1.113/-1.454

 Table 2
 Summary of X-ray diffraction data experimental

 $J_1 = J_2 = J_3 = -1.5$ cm⁻¹. Other parameters are $g_1 = g_3 = g_2 = g_4 = 2.50$, PI = 5.0% (fixed) and $TIP = 33.5 \times 10^{-4}$ cm³mol⁻¹ (fixed). It should be mentioned that the use of a simple dimer model (with two isolated dinuclear units and only a single intrasubunit coupling constant) did not lead to an acceptable fit in this case.

For any magnetostructural correlations it is necessary to have a series of comparable systems with similar structures. To the best of our knowledge there is only one other example in the literature where two six-coordinate cobalt(II) ions are bridged by a pyrazolate only,¹¹ akin to the situation in **1**. In this case a very similar coupling constant of -2.0 cm^{-1} was observed. Any comparison of the coupling between cobalt(II) ions in complexes **1**, **2** and **3** is hampered by the different metal ion coordination numbers, namely five in **1**, four and six in **2**, and six in complex **3**.

Conclusions

Two new derivatives have been added to the class of pyrazolebased ligands with imine side arms, which are best described as coupled binucleating versions of the well-known α -diimine type systems. The new ligands feature phenyl backbone substituents at the pyrazole-C⁴ and at the imine-C (R¹ = H/Ph, R² = Ph), extending the variability of substituent bulkiness for these compartmental scaffolds. Reaction of three such ligands with different backbone substitution pattern with CoCl₂ leads to distinct coordination compounds under identical conditions. HL¹ forms a dinuclear complex [L¹Co₂Cl₃(H₂O)₂(EtOH)] (1) with unusual double intramolecular (H)O-H… Cl hydrogen bonding, HL² gives a complex [(L²)₃Co₄Cl₅] (2) with ligand to metal ratio of 3:4 and with both tetrahedral and octahedral cobalt(II) ions, while HL³ yields the rectangular tetrametallic [(L³)₂Co₄Cl₆(H₂O)₅] (3) with a unique μ_4 -Cl atom encapsulated by four six-coordinate cobalt(II) ions. The combination of UV-Vis and ESI-MS data suggest, however, that species different from those seen in the solid state may be present in solution, since evidence has been obtained for a dimeriziation equilibrium between 1 and a tetranuclear complex 1' that is similar to 3. Magnetic data reveal antiferromagnetic coupling between six-coordinate cobalt(II) ions, although coupling is rather weak if mediated by a single pyrazolate or chloride bridge only, and somewhat stronger solely in the case of double pyrazolate/chloride bridging. Interaction between tetrahedral and octahedral metal ions in 2 appears to be weakly ferromagnetic, which is likely due to partial orthogonality of the magnetic orbitals.

The present work underlines the versatility of the pyrazole/imine hybrid ligands to serve as binucleating ligand scaffolds, and it shows that subtle variations in the ligand backbone can have severe influences on the topology of the resulting complexes. This is important information for the use of these ligand class in, *e.g.*, catalytic applications.

Experimental

Materials and preparation

All reactions with metal salts were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. Melting points/decomposition temperatures were determined with an OptiMelt system (Stanford Research Systems, Inc.) using open capillaries, values are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 500 spectrometer. ¹³C resonances were obtained with broad-band proton decoupling, spectra were recorded at 298 K. ¹H NMR and ¹³C NMR chemical shifts were referenced internally to solvent

signals. Mass spectra were recorded using a Finnigan MAT (FAB) using 3-nitrobenzylalcohol as a matrix, a Finnigan MAT 8200 (EI) or Bruker APEX IV (HRMS, ESI). IR spectra from KBr pellets were recorded on a Digilab Excalibur Series FTS 3000 spectrometer. Elemental analyses were performed by the analytical laboratory of the Institute of Inorganic Chemistry at Georg-August-University Göttingen using a Heraeus CHN-O-RAPID instrument or an Elementar vario EL III instrument. UV-Vis spectra were measured on a Varian Cary 5000 or an Analytic Jena Specord S 100 spectrometer in a 1 cm pathway cuvette. All reagents were purchased from commercial sources and employed without further treatment. CoCl₂ was dried under vacuum at 120 °C and 2,6-diisopropylaniline was purified by distillation prior to use. HL^1 and **C** were synthezised according to the published procedures.15,18

Synthesis of 3,5-bis(2,6-diisopropylphenyliminomethyl)-1H-4-phenylpyrazole (HL²)

A solution of dialdehyde C ($R^1 = H, R^2 = Ph$; 1.90 g, 9.50 mmol) and 2,6-diisopropylaniline (10.0 g, 57.0 mmol) in toluene (500 mL) was heated to reflux for 72 h. After the solvent and the excess of 2,6-diisopropylaniline had been removed, the crude product was crystallised from ethanol or acetone to give HL² (4.48 g, 8.60 mmol, 91%) as white crystals. Mp 120 °C. Anal. Calcd. (%) for C35H42N4, 0.5 H2O: C, 79.66; H, 8.21; N, 10.62. Found: C, 79.65; H, 8.12; N, 10.61. IR (KBr): 3450 w, 3395 w, 3213 w, 3061 w, 3026 w, 2961 vs, 2928 s, 2868 s, 1663 vs, 1625 vs, 1462 s, 1440 s, 1382 m, 1363 m, 1326 w, 1260 m, 1204 m, 1180 m, 1142 w, 1102 w, 1043 w, 1012 w, 935 w, 886 w, 801 m, 764 m, 701 m cm⁻¹. ¹H NMR (500 MHz, CDCl₃): $\delta = 1.15 - 1.16$ (24 H, d, ${}^{3}J_{HH} = 4.5$ Hz, CH₃), 2.98 (4 H, br, CH), 7.10–7.44 (11 H, m, CH^{Ar}), 8.15 (2 H, s, HC=N). ¹³C NMR (125 MHz, CDCl₃): $\delta = 23.6$ (CH₃), 28.0 (CH), 118.9 (C^{Ar}), 123.1 (CH^{Ar}), 123.2 (CH^{Ar}), 124.8 (CH^{Ar}), 128.2 (CH^{Ar}), 128.4 (CH^{Ar}), 128.5 (C^{Ar}), 130.3 (C^{Ar}), 130.5 (CH^{Ar}), 137.7 (C^{Ar}), 148.5 (C^{Ar}), 152.5 (C=N). MS (EI, 70 eV): m/z (%) = 518 $(L^+, 9), 475 (L-iPr^+, 100)$. MS (ESI⁺, CH₃CN): m/z (%) = 1059 $(L_2+Na^+, 25), 559 (L + K^+, 100), 541 (L + Na^+, 65), 519 (L + H^+, 65), 519 (L + H^+$ 72). HR-MS (ESI⁺, CH₃CN): m/z calcd for C₃₅H₄₃N₄ (L + H⁺): 519.34822; found: 519.34815.

Synthesis of 3,5-bis(2,6-diisopropylphenyliminobenzoyl-1H-4-phenylpyrazole (HL³)

A solution of diketone C ($R^1 = R^2 = Ph$; 1.00 g, 2.84 mmol) and 2,6-diisopropylaniline (3.00 g, 17 mmol) in toluene (150 mL) with a catalytic amount of trifluoroacetic acid (14 mol%) was heated to reflux for 72 h. After the solvent and the excess of 2,6-diisopropylaniline had been removed the crude product was crystallised from ethanol or acetone/hexane to give HL³ (1.78 g, 2.66 mmol, 94%) as yellow needles. Mp 138 °C. Anal. Calcd. for C47H50N4, 0.5 H2O, C2H6O: C, 81.06; H, 7.91; N, 7.72. Found: C, 80.67; H, 7.93; N, 7.78. IR (KBr): 3435 m, 3424 m, 3059 w, 3025 w, 2963 vs, 2934 m, 2868 s, 1705 m, 1626 s, 1599 m, 1588 s, 1575 m, 1497 w, 1459 m, 1447 w, 1433 s, 1383 m, 1364 s, 1322 m, 1281 w, 1255 w, 1238 w, 1220 m, 1179 w, 1151 w, 1103 w, 1074 w, 1055 w, 1043 w, 1017 w, 938 vs, 930 vs, 910 m, 800 w, 780 m, 766 s, 747 m, 725 w, 696 vs, 629 w, 533 w cm⁻¹. ¹H NMR (500 MHz, CDCl₃): $\delta = 0.93 (12 \text{ H}, \text{d}, {}^{3}J_{HH} = 6.8 \text{ Hz}, \text{CH}_{3}), 1.22 (12 \text{ H}, \text{d}, {}^{3}J_{HH} =$

6.8 Hz, CH₃), 3.33 (4 H, sept, ${}^{3}J_{HH} = 6.8$ Hz, CH), 6.32–7.66 (21 H, m, CH^{Ar}). ¹³C NMR (125 MHz, CDCl₃): $\delta = 21.9$ (CH₃), 24.0 (CH₃), 28.3 (CH), 122.7 (CH^{Ar}), 122.8 (CH^{Ar}), 126.2 (CH^{Ar}), 126.8 (CH^{Ar}), 127.1 (CH^{Ar}), 127.3 (CH^{Ar}), 127.6 (CH^{Ar}), 128.8 (CH^{Ar}), 128.9 (CH^{Ar}), 129.1 (CH^{Ar}), 130.6 (CH^{Ar}), 131.7 (C^{Ar}), 134.2 (C^{Ar}), 135.5 (C^{Ar}), 135.9 (C^{Ar}), 144.5 (C^{Ar}), 145.8 (C^{Ar}), 160.0 (C=N). MS $(ESI^+, CH_3CN): m/z \ (\%) = 1364 \ (2L + Na^+, 16), \ 693 \ (L + Na^+, 16),$ 38), 671 (L + H⁺, 100). HR-MS (ESI⁺, CH₃CN): m/z calcd for $C_{47}H_{51}N_4$ (L + H⁺): 671.41082; found: 671.41067.

General synthetic method for the preparation of complexes

To a stirred solution of HL and KO'Bu in THF (50 mL) was added dry CoCl₂. The solution was stirred for 15 h at room temperature and then evaporated to dryness. The resulting green powder was crystallised.

Synthesis of [L¹Co₂Cl₃(H₂O)₂(EtOH)] (1)

Complex 1 was prepared according to the above procedure using HL¹ (375 mg, 0.77 mmol), KO'Bu (87 mg, 0.77 mmol) and CoCl₂ (200 mg, 1.5 mmol). The resulting green powder was crystallised from wet CHCl₃/EtOH or from acetone to give purple crystals (520 mg, 0.66 mmol, 86%). Anal. Calcd. for C₃₂H₄₃N₄Co₂Cl₃(H₂O)₂(EtOH), 0.75 CHCl₃: C, 47.45; H, 6.15; N, 6.36. Found: C, 47.53; H, 6.04; N, 6.21. IR (KBr): 3413 br, 3063 w, 2963 vs, 2926 s, 2867 m, 1732 m, 1698 w, 1622 m, 1572 vs, 1486 w, 1462 m, 1440 m, 1426 m, 1383 w, 1363 m, 1328 s, 1254 w, 1235 m, 1184 m, 1102 m, 1068 w, 1057 w, 1024 w, 1007 w, 964 w, 937 w, 851 w, 801 m, 772 m, 727 m, 577 m, 450 w cm⁻¹. MS (ESI⁺, CH₃CN): m/z (%) = 1379 (L₂Co₄Cl₅⁺, 56), 1250 (L₂Co₃Cl₃⁺, 20), 1155 (L₂Co₂Cl₂+H⁺, 11), 1119 (L₂Co₂Cl⁺, 67), 1026 (L₂Co + H⁺, 23), 671 (M-Cl,2H₂O,EtOH⁺, 100), 578 (LCoCl + H⁺, 14), 485 (L + H⁺). UV-Vis (CH₂Cl₂) λ [nm] (ϵ [L mol⁻¹ cm⁻¹]): 248 (157152), 269 (145945), 531 (85), 556 (101), 587 (113), 672 (111). UV-Vis (diffuse reflectance, KBr) λ [nm]: 223, 256, 317, 533, 583, 628, 659. HR-MS (ESI+, CH₃CN): m/z calcd for C₃₂H₄₃N₄Cl₂Co₂ (M-Cl,2H₂O,EtOH⁺): 671.1524; found: 671.1528.

Synthesis of [(L²)₃Co₄Cl₅] (2)

Complex 2 was prepared according to the above procedure using HL² (200 mg, 0.39 mmol), KO'Bu (43 mg, 0.39 mmol) and CoCl₂ (100 mg, 0.77 mmol). The resulting green powder was crystallised from CH₂Cl₂, toluene or THF/CH₃CN to give green crystals (220 mg, 0.11 mmol, 86%). Anal. Calcd. for C₁₀₅H₁₂₃N₁₂Co₄Cl₅, 3 THF, CH₃CN, H₂O: C, 63,76; H, 6,83; N, 8.12. Found: C, 63.75; H, 6.81; N, 8.05. IR (KBr): 3401 br, 3061 w, 3027 w, 2962 vs, 2927 s, 2868 m, 1769 w, 1720 w, 1603 vs, 1540 w, 1461 s, 1441 m, 1383 w, 1363 w, 1326 w, 1292 w, 1255 w, 1244 w, 1179 m, 1099 w, 1057 w, 1038 m, 1018 w, 977 w, 923 w, 899 m, 844 w, 801 m, 754 m, 701 m, 583 w, 536 w, 473 w cm⁻¹. MS (FAB): m/z (%) = 1964 (M⁺, 21), 1929 (M – Cl⁺, 82), 1449 ($L_2Co_4Cl_5^+$, 29), 1318 ($L_2Co_3Cl_3^+$, 100), 1187 (L₂Co₂Cl⁺, 45), 1152 (L₂Co₂, 36). UV-Vis (CH₂Cl₂) λ [nm] (ε [L mol⁻¹cm⁻¹]): 242 (635833), 276 (655208), 580 (237), 635 (226), 688 (331). UV-Vis (diffuse reflectance, KBr) λ [nm] : 224, 284, 475, 579, 633, 688.

Synthesis of [(L³)₂Co₄Cl₆(H₂O)₅] (3)

Complex 3 was prepared according to the above procedure using HL³ (70 mg, 0.10 mmol), KO'Bu (12 mg, 0.10 mmol) and CoCl₂ (26 mg, 20 mmol). The resulting green powder was crystallised from CHCl₃/acetone or acetone to give green crystals (50 mg, 0.027 mmol, 54%). Anal. Calcd. for C₉₄H₉₈N₈Co₄Cl₆(H₂O)₅, C₃H₆O: C, 60.16; H, 5.93; N, 5.79. Found: C, 59.93; H, 6.14; N, 5.84. IR (KBr): 3375 br, 3059 w, 3027 w, 2963 vs, 2928 w, 2867 m, 1618 w, 1603 w, 1581 m, 1554 s, 1494 m, 1461 s, 1432 s, 1384 m, 1363 w, 1327 s, 1251 m, 1217 w, 1178 w, 1162 w, 1100 w, 1055 m, 1043 w, 1022 m, 978 s, 935 w, 913 w, 806 w, 779 m, 770w, 744 m, 722 w, 695 vs, 640 w, 602 w, 564 w, 539 w, 523 w, 442 w cm⁻¹. MS (ESI⁺, CH₃CN): m/z (%) = 1528 (L₂Co₂Cl₂+H⁺, 15), 1398 $(L_2Co + H^+, 12), 857 (LCo_2Cl_2^+, 29), 728 (LCo^+, 17), 671 (HL + H^+)$ 100). MS (ESI⁻, CH₃CN): m/z (%) = 798 (LCoCl₂⁻, 30), 669 (L⁻, 100). MS (FAB): m/z (%) = 1435 (L₂CoCl⁻, 20), 1399 (L₂Co⁻, 47), 764 (LCoCl, 90), 671 (HL + H⁺, 98), 627 (L-*i*Pr⁺, 100). UV-Vis $(CH_2Cl_2) \lambda$ [nm] (ϵ [L mol⁻¹cm⁻¹]): 239 (617491), 262 (701053), 561 (271), 584 (307), 671 (305). UV-Vis (diffuse reflectance, KBr) λ [nm] : 224, 289, 562, 584, 673.

Magnetic susceptibility measurements

Susceptibility measurements were carried out with a Quantum-Design MPMS-5S SQUID magnetometer equipped with a 5 Tesla magnet in the range from 295 to 2.0 K. The powdered samples were contained in a gel bucket and fixed in a non-magnetic sample holder. Each raw data file for the measured magnetic moment was corrected for the diamagnetic contribution of the sample holder and the gel bucket. The molar susceptibility data were corrected using the Pascal constant and the increment method according to Haberditzel.

X-Ray crystallography

X-Ray data were collected on a STOE IPDS II diffractometer (graphite monochromated Mo K α radiation, $\lambda = 0.71073$ Å) by use of ω scans at -140 °C. The structures of HL², HL³, **1**, **2**, and **3** were solved by direct methods and refined on F^2 using all reflections with SHELX-97.⁴⁰ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å². Face-indexed absorption corrections were performed numerically with the program X-RED.⁴¹ One CHCl₃ in **1** is disordered about a crystallographic centre of inversion and was refined with a fixed occupancy factor of 0.5. SADI restraints ($d_{C...CI}$) were applied to model the disorder. In **2** two acetonitrile and one THF were refined at half occupancy.

In **3** the positions above and below the plane {N₂CoCl₂} are statistically occupied by metal bound water molecules and chlorine atoms. These oxygen and chlorine atoms were refined at half occupancy. The unit cell of **3** contains disordered acetone solvent molecules, for which no satisfactory model for the disorder was found. For further refinement, the contribution of the missing solvent molecules (249.5 Å³, electron count 46) was subtracted from the reflection data by the SQUEEZE⁴² routine of the PLATON⁴³ program.

Acknowledgements

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amounts of CoCl₂. Only a diamagnetic correction was considered for the sample holder, but our estimate for sample holder contributions to the *PI* is less than 0.02 mol%.

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