Novel Dinucleating Ligand Systems Containing Two Adjacent Coordination Compartments of the Potential Triamidoamine-Type – Nickel(II) and Cobalt(II) Coordination Chemistry

Silke Buchler, Franc Meyer*, Albrecht Jacobi, Peter Kircher, and Laszlo Zsolnai

Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

* Reprint requests to Dr. F. Meyer. Fax: (0049) 6221 545707 E-mail: franc@sun0.urz.uni-heidelberg.de

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The preparation of novel dinucleating pyrazolate ligands $H_5L^3 - H_5L^8$ carrying chelating side arms with appending secondary amine functions is reported. Following different synthetic routes, either CH₂CF₃, C₆H₂F₃, or C₆F₅ moieties can be introduced as substituents at the terminal nitrogen atoms. These systems are reminiscent of two coupled coordination compartments of the potential triamidoamine-type. Crystallographic analyses of a series of bimetallic complexes of the CH₂CF₃-substituted ligand H₅L⁴ with NiCl₂ and CoCl₂ reveal manifold coordination modes in the solid state, resulting from the facile detachment of a single or several N-donor sites from the metal centers. Coordination number sets {4/6} (in H₅L⁴Co₂Cl₄) and {5/6} (in H₄L⁴Ni₂Cl₃, H₄L⁴Co₂Cl₃ and H₅L⁴Ni₂Cl₄) are thus observed. In the non-deprotonated H₅L-type systems the remaining protons are found to be scavenged by a pyrazolate-N (in H₅L⁴Ni₂Cl₄) or an amine function of a ligand side arm (in H₅L⁴Co₂Cl₄).

Introduction

Dinuclear transition metal complexes have received considerable attention in the past several vears, mainly due to the increasing interest in cooperative effects between individual metal centers [1, 2]. One fundamental approach to achieve this sought-after cooperativity is the design of dinucleating ligand matrices that hold the two metal ions in close proximity by providing adjacent coordination compartments with suitable sets of donor functions [3]. In this regard we have recently studied a series of pyrazolate-based bimetallic complexes. in which the coordination spheres of the metal ions as well as the accessible range of metal-metal separations can be selectively altered by appropriate changes of the chelating substituents attached to the heterocycle [4 - 6]. Among these, the representative type I ligands HL^1 and HL^2 can be viewed as two tran-type coordination compartments [tran = tris-(aminoalkyl)amine] coupled by a pyrazole moiety (Scheme 1) [4]. However, while these systems gave rise to a diverse chemistry of dinuclear complexes of (usually late) divalent 3d transition metals [6], they proved less suited for stabilizing complexes of



Scheme 1. Pyrazole-based type I and type II dinucleating ligand systems.

early 3d transition metal ions and for allowing multielectron redox chemistry of the bimetallic site. A class of ligands closely related to the tran systems are the mononucleating triamidoamine anions $\{[RN(CH_2)_n]_3N\}^{3-}$, which have been intensively studied by Verkade *et al.* [7], Schrock *et al.* [8], and others [9]. These ligands can bind to a variety of transition metals in different oxidation states, in particular in oxidation states 3+ and higher, and turned out to be especially suited for stabilizing transition metals with relatively low d electron count [8].

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Scheme 2. Synthesis of type II ligands $H_5L^3 - H_5L^6$.

Moreover, the fixation of dinitrogen achieved within di- and oligonuclear arrangements of such triamidoamine molybdenum and uranium complexes underlines the special capabilities that cooperating metal ions in multinuclear arrangements might offer for the activation of small substrate molecules [10].

In this context we intended to prepare novel type II dinucleating ligand frameworks which have the potential to provide two adjacent coordination pockets, each bearing similarity to the mononucleating triamidoamine compartments. The present contribution reports a first synthetic strategy giving access to such systems II, and it describes the basic coordination behavior of one selected ligand towards cobalt(II) and nickel(II) chloride in comparison to the corresponding complexes of L^1 and L^2 .

Results and Discussion

Ligand synthesis

The known synthetic route for the preparation of type I ligands L^1 and L^2 starts from pyrazole-3,5-dicarboxylic acid. This is first converted into the corresponding bis(acid chloride), and subsequently treated with the appropriate secondary amine. The resulting bis(amide) is finally reduced using an excess of LiAlH₄ [4, 11]. With the aim of limiting the preparative effort and the number of synthetic steps we decided to adapt this established strategy also for the synthesis of the new systems II (Scheme 2). This implies the necessity to protect the terminal sec-

ondary amine functions of the employed triamine in order to selectively react its central N atom with the acid chloride. We first chose the trifluoroacetyl protecting group that is conveniently introduced [12] by treating diethylenetriamine or dipropylenetriamine with ethyl trifluoroacetate to give **1a**, **b**, respectively. Its electron withdrawing properties now allow for a selective coupling of the central N atom of **1a**, **b** with the pyrazole moiety to afford **2a**, **b**, and the subsequent reduction step not only transforms the newly formed amide linkages but at the same time reduces the trifluoroacetyl groups to yield the type **II** ligands H_5L^3 and H_5L^4 carrying trifluoroethyl substituents at the terminal amine functions.

Altogether the trifluoroacetyl group serves two purposes, *i. e.* it first acts as a protecting group during the coupling reaction and is then converted into the requisite terminal substituent at the amine donors without increasing the overall number of synthetic steps. In addition, the same procedure may be used to attach long chain fluorinated substituents at the ligand core by employing appropriate perfluoroalkylcarboxy protecting groups (which we have exemplary proved by starting from the heptafluorobutyryl protected triamines), a prospect that might possibly be of interest in the view of a future modification of the solubility of resulting complexes [13].

As electron-withdrawing pentafluorophenyl substituents at the terminal nitrogen atoms proved particularly useful for the formation of the metal-amido bond in triamidoamine chemistry [8, 14], we also



Table I. Selected atom distances [Å] and bond angles [°] for $L^1Ni_2Cl_3$.

1.945(6)	Ni1-N3	2.188(6)
2.104(7)	Ni1-Cl1	2.406(2)
2.282(2)	Ni2-N2	1.951(6)
2.217(6)	Ni2-N6	2.103(7)
2.288(2)	Ni2-Cl1	2.422(2)
1.353(8)	Ni1…Ni2	3.829
79.1(2)	N1-Ni1-N4	99.6(3)
87.9(2)	N1-Ni1-Cl2	156.8(2)
86.7(3)	N3-Ni1-Cl1	164.7(2)
94.6(2)	N4-Ni1-Cl1	103.6(2)
102.3(2)	Cl1-Ni1-Cl2	94.21(9)
79.2(2)	N2-Ni2-N6	99.5(3)
87.9(2)	N2-Ni2-Cl3	153.1(2)
86.0(2)	N5-Ni2-Cl1	166.0(2)
95.1(2)	N6-Ni2-Cl1	101.6(2)
106.3(2)	Cl1-Ni2-Cl3	94.06(8)
129.4(4)	Ni2-N2-N1	128.6(4)
104.94(8)		
	$\begin{array}{c} 1.945(6)\\ 2.104(7)\\ 2.282(2)\\ 2.217(6)\\ 2.288(2)\\ 1.353(8)\\ 79.1(2)\\ 87.9(2)\\ 86.7(3)\\ 94.6(2)\\ 102.3(2)\\ 79.2(2)\\ 87.9(2)\\ 86.0(2)\\ 95.1(2)\\ 106.3(2)\\ 129.4(4)\\ 104.94(8) \end{array}$	1.945(6) Ni1-N3 2.104(7) Ni1-Cl1 2.282(2) Ni2-N2 2.217(6) Ni2-N6 2.288(2) Ni2-Cl1 1.353(8) Ni1-···Ni2 79.1(2) N1-Ni1-N4 87.9(2) N1-Ni1-Cl2 86.7(3) N3-Ni1-Cl1 94.6(2) N4-Ni1-Cl1 102.3(2) Cl1-Ni1-Cl2 79.2(2) N2-Ni2-N6 87.9(2) N2-Ni2-Cl3 86.0(2) N5-Ni2-Cl1 95.1(2) N6-Ni2-Cl1 106.3(2) Cl1-Ni2-Cl3 129.4(4) Ni2-N2-N1 104.94(8) Ni2-N2-N1

set out to introduce C_6F_5 moieties as R groups in our type II ligands. The necessary building blocks 1c, d are readily available by reaction of the respective triamine with hexafluorobenzene [15], and can selectively be attached to the pyrazole nucleus to give 2c, d. However, the final reduction step in these cases not only transforms all amide functions, but simultaneously leads to partial nucleophilic substitution of the aryl-bound fluoride by hydride. If reaction conditions are controlled carefully, this can be limited to a quite selective replacement of solely the *meta*-fluorine atoms, thus leading to the 2,4,6trifluorophenyl-substituted potential ligands H_5L^5 and H_5L^6 in reasonable purity (Scheme 2).

A different route not requiring such a harsh reduction step had to be developed in order to obtain the C₆F₅-substituted compounds. 3,5-bis(chloromethyl)pyrazole turned out to be a suitable starting material, if the potentially nucleophilic NH function of the heterocycle is protected by a tetrahydropyranyl (THP) group prior to attaching the sidearm components **1c**, **d** [16]. The protecting group is finally removed by treatment with acid to yield H_5L^7 , H_5L^8 (Scheme 3).





Fig. 1. Molecular structure of $L^1Ni_2Cl_3$.

A series of novel dinucleating ligand systems reminescent of two coupled coordination compartments of potential triamidoamine-type are thus available. A first glance at their coordination potential is obtained from some coordination compounds of the selected ligand H_5L^4 , where the ligand acts as a simple polyamine donor.

Synthesis and structural characterization of cobalt(II) and nickel(II) complexes

With the aim of probing the coordination potential of the new systems in comparison to related complexes of L^1 and L^2 , we investigated coordination compounds of H_5L^4 with cobalt(II) and nickel(II) chloride. The structures of $L^1Co_2Cl_3$ and $L^2Co_2Cl_3$ have been reported previously [4]. We now synthesized the analogous systems $L^1Ni_2Cl_3$ and $L^2Ni_2Cl_3$ from the respective ligands, which were deprotonated prior to their subsequent reaction with NiCl₂. The formation of coordination compounds is inferred from the mass spectra, which show dominant peaks corresponding to the fragment ions $[LNi_2Cl_2]^+$. The molecular structures of the new complexes were determined by X-ray crystallography and are depicted in Figs 1 and 2; repre-

for $L^2Ni_2Cl_3$. Nil-N1 1.962(2)Ni1-N2 2.195(3)Nil-N4 2.083(3)Ni1-Cl1 2.4632(8) N1-N1^{#1} Ni1-Cl2 2.2852(9)1.360(5) $Ni1 \cdots Ni1^{\#1}$ 3.917 N1-Ni1-N2 78.6(1)N1-Ni1-N4 101.6(1)159.1(1) N1-Ni1-Cl1 86.3(1) N1-Ni1-Cl2 N2-Ni1-N4 98.3(1) N2-Ni1-Cl1 160.4(1)93.7(1) 97.0(1) N2-Ni1-Cl2 N4-Ni1-Cl1 N4-Ni1-Cl2 98.8(1)Cl1-Ni1-Cl2 96.1(1)Nil-Cll-Nil^{#1} Ni1-N1-N1#1 129.8(1)105.3(1)

Table II. Selected atom distances [Å] and bond angles [°]



Fig. 2. Molecular structure of L²Ni₂Cl₃.

sentative atom distances and bond angles are listed in Tables I and II, respectively. $L^1Ni_2Cl_3$ crystallizes in the monoclinic space group $P2_1/c$ with 4 molecular entities in the unit cell, while $L^2Ni_2Cl_3$ is found to crystallize in the tetragonal space group $P4_32_12$ with 4 molecules in the unit cell.

Similar to the results for the known cobalt(II) systems [4], the nickel ions are found to be fivecoordinate with two ligand side arms remaining uncoordinated. This is in accordance with previous observations for related mononuclear complexes of tran-type ligand systems, where in the case of N,Ndialkylated terminal amino donors the coordination of the metal centers is restricted to five-coordination for steric reasons [17]. Referring to the angular structural parameter $\tau = (\beta - \alpha)/60$, where α and β represent two basal angles with $\beta > \alpha$ [18], the coordination geometry around the nickel ions in L¹Ni₂Cl₃ ($\tau = 0.13/0.22$ for Ni1/Ni2) and

Table III.	Selected	atom	distances	[A]	and	bond	angles
[°] for H ₄	$L^4Ni_2Cl_3$						

Nil-Nl	1.991(3)	Ni1-N3	2.191(3)
Nil-N4	2.235(3)	Ni1-N5	2.182(3)
Ni1-Cl1	2.567(1)	Ni1-Cl3	2.347(1)
Ni2-N2	1.973(3)	Ni2-N6	2.178(3)
Ni2-N7	2.066(3)	Ni2-Cl1	2.477(1)
Ni2-Cl2	2.312(1)	N1-N2	1.360(4)
Ni1…Ni2	3.991		
N1-Ni1-N3	79.5(1)	N1-Ni1-N4	88.6(1)
N1-Ni1-N5	93.5(1)	N1-Ni1-Cl1	84.90(9)
N1-Ni1-Cl3	177.0(1)	N3-Ni1-N4	97.3(1)
N3-Ni1-Cl1	163.02(8)	N3-Ni1-Cl3	98.23(9)
N4-Ni1-Cl1	88.94(9)	N4-Ni1-Cl3	89.69(9)
N5-Ni1-N3	90.8(1)	N5-Ni1-N4	171.9(1)
N5-Ni1-Cl1	83.45(9)	N5-Ni1-Cl3	88.49(9)
Cl2- Ni1-Cl1	97.57(4)	N2-Ni2-N6	79.38(1)
N2-Ni2-N7	107.56(1)	N2-Ni2-Cl1	86.51(9)
N2-Ni2-Cl2	154.58(9)	N6-Ni2-Cl1	160.60(8)
N6-Ni2-Cl2	94.21(9)	N7-Ni2-N6	95.49(1)
N7-Ni2-Cl1	101.46(9)	N7-Ni2-Cl2	97.48(1)
Cl2-Ni2-Cl1	92.88(4)		



Fig. 3. Molecular structure of H₄L⁴Ni₂Cl₃.

 $L^2Ni_2Cl_3$ ($\tau = 0.02$) can be described as predominantly SPY-5 (a perfect TB-5 structure is associated with $\tau = 1$, while $\tau = 0$ is expected for an ideal SPY-5 geometry). The distance Ni…Ni amounts to 3.829 ($L^1Ni_2Cl_3$) and 3.917 Å ($L^2Ni_2Cl_3$).

As anticipated, treatment of the new ligand H_5L^4 with two equivalents of NiCl₂ or CoCl₂ in the presence of an external base affords coordination compounds $H_4L^4N_i_2Cl_3$ and $H_4L^4Co_2Cl_3$, whose formation is again corroborated by mass spectro-

Col-N1	2.024(2)	Col-N3	2.257(2)
Col-N4	2.240(2)	Co1-N5	2.282(2)
Col-Cll	2.350(8)	Co1-Cl3	2.576(9)
Co2-N2	1.986(2)	Co2-N6	2.291(2)
Co2-N7	2.117(2)	Co2-Cl2	2.316(8)
Co2-Cl3	2.483(9)	N1-N2	1.370(3)
Co1…Co2	3.992		
N1-Co1-N3	77.58(8)	N1-Co1-N4	92.23(9)
N1-Co1-N5	89.13(9)	N1-Co1-Cl1	176.06(6)
N1-Co1-Cl3	85.74(6)	N3-Co1-N5	97.00(8)
N3-Co1-Cl1	98.82(6)	N3-Co1-Cl3	162.35(6)
N4-Co1-N3	89.82(8)	N4-Co1-N5	173.17(8)
N4-Co1-Cl1	89.35(7)	N4-Co1-Cl3	85.06(6)
N5-Co1-Cl1	89.73(7)	N5-Co1-Cl3	88.38(6)
Cl1-Co1-Cl3	98.00(3)	N2-Co2-N6	77.00(8)
N2-Co2-N7	110.75(9)	N2-Co2-Cl2	148.54(7)
N2-Co2-Cl3	88.35(6)	N6-Co2-Cl2	92.95(6)
N6-Co2-Cl3	161.23(6)	N7-Co2-N6	93.14(9)
N7-Co2-Cl2	99.38(7)	N7-Co2-Cl3	103.10(7)

Table IV. Selected atom distances [Å] and bond angles [°] for $H_4L^4Co_2Cl_3$.



Fig. 4. Molecular structure of H₄L⁴Co₂Cl₃.

metry (dominant peaks with m/z corresponding to $[H_4L^4Ni_2Cl_2]^+$ and $[H_4L^4Co_2Cl_2]^+$, respectively). Magnetic moments per metal ion at room temperature of 2.87 \pm 0.10 μ_B ($H_4L^4Ni_2Cl_3$) and 4.35 \pm 0.07 μ_B ($H_4L^4Co_2Cl_3$) confirm the presence of highspin nickel(II) and cobalt(II), respectively, with the common orbital angular momentum contributions in the latter case [19]. These complexes can be obtained in crystalline form by slow diffusion of light petroleum into CH₂Cl₂ ($H_4L^4Ni_2Cl_3$) or CHCl₃ ($H_4L^4Co_2Cl_3$) solutions. Apart from the fact that

Table V. UV/Vis data of the complexes; λ /nm (ε /M⁻¹cm⁻¹).

H ₄ L ⁴ Ni ₂ Cl ₃ ^a	410 (192), 686 (72), 1130 (43)
H ₄ L ⁴ Ni ₂ Cl ₃ ^b	421,690
$H_4L^4Co_2Cl_3^{a}$	538 (48), 581 (50), 635 (51)
$H_4L^4Co_2Cl_3$ ^b	588, 639, 682
$H_5L^4Ni_2Cl_4$ ^a	413 (143), 690 (49), 1130 (31)
H ₅ L ⁴ Ni ₂ Cl ₄ ^b	415, 690, 1050
$H_5L^4Co_2Cl_4$ ^a	596 (117), 639 (156), 678 (147)
H ₅ L ⁴ Co ₂ Cl ₄ ^b	585, 642, 685

^a in EtOH; ^b dispersion in nujol.

some of the differing solvent as used for crystallization is included in the crystal lattice, both compounds are isotypic and crystallize in the monoclinic space group $P2_1/c$. Their molecular structures are depicted in Figs 3 and 4, representative atom distances and bond angles are given in Tables III and IV.

Unexpectedly, both H₄L⁴Ni₂Cl₃ and H₄L⁴Co₂-Cl₃ feature asymmetric dinuclear cores in which one metal atom [Ni1/Co1] is six-coordinated in a distorted OC-6 surrounding while the second metal center again remains five-coordinate [Ni2/Co2; $\tau =$ 0.10/0.21] leaving a single side arm dangling. This finding is surprising, as there is no obvious geometric or electronic distinction between the two metal centers spanned by the symmetric dinucleating ligand framework that would restrict an increase in coordination number to only one of them. Furthermore, a related pyrazolate-based dinickel(II) complex providing terminal thioether donor functions at the ligand side arms gave a symmetric complex with both metal centers in OC-6 environments [5a], so that steric reasons appear not to be responsible for the present results. However, the structural asymmetry found for H₄L⁴Ni₂Cl₃ and H₄L⁴Co₂Cl₃ in the solid state closely resembles the unusual oligomerization observed for some related dinickel(II) complexes of pyrazolate ligands with fewer chelating donor functions, also proceeding via a partial increase in coordination number from five to six [20].

While the UV/Vis spectra of $H_4L^4Ni_2Cl_3$ are quite similar in solution (EtOH) and in the solid state (dispersion in nujol), the spectra of $H_4L^4Co_2Cl_3$ undergo considerable changes upon dissolving of the complex in EtOH (Table V), indicative of a different structure in solution. Closer inspection reveals that the solution optical absorptions of $H_4L^4Co_2Cl_3$ bear resemblance to those previously reported for $L^2Co_2Cl_3$ [4], thus suggesting detachment of a



Scheme 4. Constitution of $H_5L^4Ni_2Cl_4$ in the solid state.

further ligand side arm to give two five-coordinated metal centers in the present case, too.

When H_5L^4 is treated with the same metal salts in the absence of an external base, different complexes with empirical formula $H_4LNi_2Cl_3 \cdot HCl$ and $H_4LCo_2Cl_3 \cdot HCl$ are formed due to the presence of one additional equivalent of HCl. Again, magnetic moments per metal ion at room temperature of $3.21 \pm 0.01 \ \mu_B \ (H_5L^4Ni_2Cl_4)$ and $4.39 \pm 0.05 \ \mu_B \ (H_5L^4Co_2Cl_4)$ confirm the presence of highspin nickel(II) and cobalt(II), respectively. Unique structures in the solid state were revealed by X-ray diffraction analyses for both of these systems.

Single crystals of H₅L⁴Ni₂Cl₄ are obtained by layering a solution of the complex in CH₂Cl₂ with Et₂O. The compound crystallizes in the triclinic space group $P\bar{1}$ with eight molecular entities (four independent bimetallic molecules) in the unit cell [21]. Unfortunately, the quality of the crystallographic analysis was poor, and we therefore refrain from any detailed discussion of the structure. However, the basic constitution of H₅L₄Ni₂Cl₄ in the solid state could be established unequivocally and is given in Scheme 4. In this case the pyrazolate core has lost its bridging coordination mode and is detached from one of the nickel ions to be left in monodentate binding to the second metal center. The latter is found in an approximate OC-6 environment, while the detached nickel ion exhibits only five-coordination. The additional proton is most likely bound to the available second N-atom of the heterocycle, as depicted in Scheme 4.

Blue crystals of the analogous complex H_5L^4 -Co₂Cl₄ are obtained by layering a solution in CH₂Cl₂ with light petroleum. The compound crystallizes in the triclinic space group $P\bar{1}$ with two molecular entities in the unit cell. Its molecular structure is depicted in Fig. 5, selected atom distances and bond angles are given in Table VI.

Interestingly the dinuclear framework consists of a six-coordinate Co1 atom (angles between *trans* donors in the range 161.7 - 174.4°) next to a fourcoordinate near-tetrahedral Co2 center. All amine

Table VI. Selected atom distances [Å] and bond angles [°] for $H_5L^4Co_2Cl_3$.

Col-N1	2.049(3)	Col-N6	2.224(3)
Col-N7	2.238(3)	Col-N8	2.223(3)
Col-Cl1	2.343(1)	Co1-Cl2	2.703(1)
Co2-N2	1.998(3)	Co2-Cl2	2.291(1)
Co2-Cl3	2.271(1)	Co2-Cl4	2.224(1)
N1-N2	1.375(3)	Co1···Co2	3.751
N1-Co1-N6	78.99(10)	N1-Co1-N7	86.37(10)
N1-Co1-N8	94.84(10)	N1-Co1-Cl1	174.41(8)
N1-Co1-Cl2	86.03(7)	N6-Co1-N7	98.93(10)
N6-Co1-Cl1	98.67(7)	N6-Co1-Cl2	161.70(7)
N7-Co1-Cl1	89.00(8)	N7-Co1-Cl2	90.48(8)
N8-Co1-N6	91.03(10)	N8-Co1-N7	170.01(11)
N8-Co1-Cl1	90.27(8)	N8-Co1-Cl2	79.72(8)
Cl1-Co1-Cl2	97.15(4)	N2-Co2-Cl2	100.59(8)
N2-Co2-Cl3	108.25(8)	N2-Co2-Cl4	111.11(8)
Cl3-Co2-Cl2	112.02(4)	Cl4-Co2-Cl2	114.85(4)
Cl4-Co2-Cl3	109.58(5)	Co2-Cl2Co1	97.04(3)



Fig. 5. Molecular structure of H₅L⁴Co₂Cl₄.

donors of one ligand side arm thus remain uncoordinated and dangling. Its tertiary nitrogen atom N3 has picked up the surplus proton that could be located as a hydrogen bridge to the cobalt-bound Cl3 atom $[d(N3\cdotsCl3) = 3.14 \text{ Å}]$. Such hydrogen bonding interactions between N-H donors and metal-bound chlorine have been recognized to be a common phenomenon [22]. All Co2-Cl distances are very similar [in the range 2.224(1) - 2.291(1) Å], while the bond length Co1-Cl2 is much longer [2.703(1) Å] and causes the Cl-bridge to exhibit distinct asymmetry. The metal-metal distance amounts to 3.75 Å, and as expected for a rather unstrained bimetallic core the two cobalt ions are situated roughly within the plane of the pyrazolate heterocycle (distance 0.08 and 0.35 Å).

A dominant peak in the mass spectrum of $H_5L^4Co_2Cl_4$ at m/z = 869 corresponding to the composition $[H_4L^4Co_2Cl_2]^+$ is indicative of facile loss of both one equivalent of HCl and a chloride ion from the complex. However, the UV/Vis spectrum is similar in EtOH and for a dispersion in nujol (Table V), thus suggesting similar structures in solution and in the solid state. Furthermore the solid state optical absorption spectra of $H_5L^4Co_2Cl_4$, and $H_4L^4Co_2Cl_3$ (see above) are comparable, and they thus seem to be dominated by the ligand-field transitions of the near-octahedral Co(II) ion.

Conclusions

Following a previously established route for the synthesis of pyrazolate-based multidentate amine ligands, novel compartemental ligand systems have been prepared which feature secondary amines at the appending side arms and thus provide two adjacent coordination compartments reminiscent of the triamidoamine-type. The crucial synthetic step is the use of trifluoroacetyl or pentafluorophenyl moieties as amine protecting groups and at the same time as precursors for the terminal amine substituents. Either CH_2CF_3 or $C_6H_2F_3$ groups can be introduced by this way. The related systems bearing C₆F₅ substituents at the terminal N atoms have been made available via an alternative synthetic strategy. The coordination potential of one selected new ligand H₅L⁴ towards late transition metals turned out to be manifold and flexible because of the facile detachment of a single or even several donor atoms from the metal centers. Consequently an unambiguous elucidation of the structure of these complexes relies on single crystal X-ray crystallography. Coordination numbers $\{4/6\}$ (in H₅L⁴Co₂Cl₄) and $\{5/6\}$ (in H₄L⁴Ni₂Cl₃) $H_4L^4Co_2Cl_3$ and $H_5L^4Ni_2Cl_4$) have been observed in the solid state. However, UV/Vis absorption spectraindicate the likely presence of a different solution structure in the case of $H_4L^4Co_2Cl_3$. Complexes $H_4L^4M_2Cl_3$ form from the ligand and an appropriate metal dichloride in the presence of external

base. While five-coordination of the metal centers in the related systems L¹Ni₂Cl₃ and L²Ni₂Cl₃ can be rationalized on the basis of steric constraints, the reason for the non-coordination of a single side arm N-donor in both H₄L⁴Ni₂Cl₃ and H₄L⁴Co₂Cl₃ is less obvious. In the absence of external base an additional chloride ion coordinates to the bimetallic system and the surplus proton is scavenged by the dinuclear core in a variable manner. In H₅L⁴Ni₂Cl₄ this proton is presumably accommodated by one of the pyrazolate-N forcing the heterocycle to give up its bridging coordination mode. On the other hand, in $H_5L^4Co_2Cl_4$ the proton is bound to one ligand side arm N-donor, which finally leaves this side arm completely uncoordinated causing fourcoordination of the respective metal center. Future work is directed towards the synthesis and study of amido-metal complexes of the new ligand systems.

Experimental

General procedures and methods

All manipulations were carried out under an atmosphere of dry nitrogen by employing standard Schlenk techniques. Solvents were dried according to established procedures. HL¹ and HL² were synthesized according to the reported method [4, 11]. Microanalyses: Mikroanalytische Laboratorien des Organisch-Chemischen Instituts der Universität Heidelberg. - IR spectra: Perkin-Elmer 983G. - FAB-MS spectra: Finnigan MAT 8230. -UV/Vis spectra: Perkin-Elmer Lambda 19. - NMR spectra: Bruker AC 200 at 200.13 (¹H) and 50.32 (¹³C) MHz; solvent signal as chemical shift reference (CDCl₃ $\delta_{\rm H}$ 7.27 $\delta_{\rm C}$ 77.0; D₆-acetone $\delta_{\rm H}$ 2.04 $\delta_{\rm C}$ 29.8). – Magnetic measurement: Bruker Magnet B-E 15 C8, field-controller B-H 15, Sartorius micro balance M 25 D-S. Experimental susceptibility data were corrected for the underlying diamagnetism.

1a, b: Ethyl trifluoroacetate was added to a solution of the triamine [diethylenetriamine (2.1 g, 20.0 mmol) or dipropylenetriamine (2.7 g, 20.0 mmol), respectively] in THF and the mixture was heated overnight. After removal of all volatile material the products **1a, b** remain as white solids. **1a** [12]: yield (5.9 g (19 mmol, 95%). ¹H NMR (D₆-acetone): δ = 1.46 (s, 1H, NH), 2.86 (t, ³J_{HH} = 5.9 Hz, 4H, CH₂), 3.44 (t, ³J_{HH} = 5.9 Hz, 4H, CH₂), 7.04 (s, 2H, NH). ¹³C{¹H} NMR (D₆-acetone): δ = 39.7 (CH₂), 47.7 (CH₂), 116.2 (q, ¹J_{CF} = 286 Hz, CF₃), 158.7 (q, ²J_{CF} = 20 Hz, CO). ¹⁹F NMR (D₆-acetone): δ = -77.2. MS (EI) *m*/*z* (%) = 296 (7) [M⁺+1], 169 (87) [M⁺-CF₃CONHCH₂], 140 (100) [CF₃CONHCH₂CH₂⁺].

 $C_8H_{11}F_6N_3O_2$ (295.2)

Calcd C 32.6 H 3.8 N 14.2%, Found C 32.0 H 3.9 N 13.6%.

1b: yield (6.4 g, 19.8 mmol, 99%). ¹H NMR (D₆-ace-

tone): $\delta = 1.54$ (s, 1H, NH), 1.77 (quint., ${}^{3}J_{HH} = 6.2$ Hz, 4H, CH₂), 2.76 (t, ${}^{3}J_{HH} = 6.2$ Hz, 4H, CH₂), 3.48 (t, ${}^{3}J_{HH} = 6.2$ Hz, 4H, CH₂), 3.48 (t, ${}^{3}J_{HH} = 6.2$ Hz, 4H, CH₂), 8.22 (s, 2H, NH). ${}^{13}C{}^{1}H$ NMR (D₆-acetone): $\delta = 27.6$ (CH₂), 38.9 (CH₂), 47.6 (CH₂), 116.0 (q, ${}^{1}J_{CF} = 286$ Hz, CF₃), 157.0 (q, ${}^{2}J_{CF} = 36$ Hz, CO). ${}^{19}F$ NMR (D₆-acetone): $\delta = -77.9$. MS (EI) m/z (%) = 323 (10) [M⁺+1], 183 (87) [M⁺-CF₃CONHCH₂CH₂], 154 (100) [CF₃CONH(CH₂)₃⁺], 126 (100) [CF₃CONHCH₂⁺].

 $C_{10}H_{15}F_6N_3O_2$ (323.2)

Calcd C 37.2 H 4.7 N 13.0%, Found C 36.5 H 4.5 N 12.2%.

Ligand H₅L³: Pyrazole-3,5-dicarboxylic acid monohydrate (2.0 g, 11.5 mmol) was converted into 3,5-bis-(chloroformyl)pyrazole by the usual reaction with thionyl chloride (100 cm³). It was taken up in THF (100 ml) and treated dropwise with a solution of 1a (7.1 g, 24.0 mmol) and triethylamine (6.6 g, 92 mmol) in THF (100 ml). After stirring overnight, a saturated aqueous sodium chloride solution was added. The phases were separated and the THF phase was dried over MgSO₄ and filtered. THF was removed under vacuum, the oily residue was taken up in THF and filtered again. After evaporation of the solvent the product 2a remained as a yellow solid, ¹H NMR (D₆-acetone): $\delta = 3.62$ (t, ${}^{3}J = 5.4$ Hz, 8H, CH₂), 3.65, 4.00 (2t, ${}^{3}J$ = 5.4 Hz, 8H, E-/Z-CH₂), 7.05 (s, 1H, $pz-H^4$), 8.81 (s, 4H, NH). ${}^{13}C{}^{1}H{}$ NMR (D₆-acetone): $\delta = 45.8 \text{ (CH}_2), 46.2 \text{ (CH}_2), 47.7 \text{ (CH}_2), 109.1 \text{ (pz-C}^4),$ 116.5 (q, ${}^{1}J_{CF}$ = 285 Hz, CF₃), 142.4 (pz-C^{3/5}), 157.5 (q, $^{2}J_{CF} = 36$ Hz, COCF₃), 163.2 (CO). ¹⁹F NMR (D₆-acetone): $\delta = -77.7$. MS (FAB+) m/z (%) = 711 (62) [M⁺+1], 416 (100) $[M^+-N](CH_2)_2NHCOCF_3]_2$. A solution of this compound 2a (8.1 g, 11.0 mmol) in THF was added dropwise to a suspension of LiAlH₄ (1.9 g, 5.0 mmol) in THF at room temperature. The mixture was heated to reflux for 4 h, stirred overnight and hydrolysed by the dropwise addition of water. The precipitate was filtered off and washed several times with THF. The combined organic phases were dried over MgSO4 and evaporated to dryness to yield H₅L³ (6.7 g, 10.7 mmol) as a yellowish oil. IR (film): $\tilde{\nu}_{max}/cm^{-1} = 3289(s), 2937(s), 2837(s),$ 1566(w), 1454(w), 1351(w), 1268(s), 1161(s), 947(m), 821(m), 661(m).¹H NMR (CDCl₃): $\delta = 1.86 (s, 4H, NH),$ 2.59 (t, ${}^{3}J = 5.3$ Hz, 8H, CH₂), 2.75 (t, ${}^{3}J = 5.3$ Hz, CH₂), $3.09 (q, {}^{3}J_{HF} = 9.4 Hz, CH_{2}CF_{3}), 3.63 (s, 4H, CH_{2}), 5.95$ (s, 1H, pz-H⁴). ¹³C{¹H} NMR (CDCl₃): δ = 46.6 (CH₂), 48.5 (CH₂), 50.0 (q, ${}^{2}J_{CF}$ = 31 Hz, CH₂CF₃), 53.6 (CH₂), 102.9 (pz-C⁴), 125.3 (q, ${}^{1}J_{CF}$ = 277 Hz, CF₃), pz-C^{3/5} not observed. ¹⁹F NMR (CDCl₃): δ = -72.2. MS (FAB+): m/z (%) = 627 (100) [M⁺+1], 514 (78) [M⁺-CF₃CH₂NHCH₂], 360 (54) [M⁺-N[(CH₂)₂NHCH₂CF₃]₂].

 $C_{21}H_{34}F_{12}N_8$ (626.5)

Calcd C 40.3 H 5.5 N 17.9%,

Found C 40.3 H 6.0 N 17.8%.

Ligand H_5L^4: Starting from pyrazole-3,5-dicarboxylic acid monohydrate (2,7 g, 15.5 mmol) and 1b (10.0 g, 31.0 mmol) the amide 2b (23.0 g, 30.0 mmol) was prepared as described for 2a. ¹H NMR (D₆-acetone): δ = 1.94 (quint, ${}^{3}J = 6.0$ Hz, 8H, CH₂), 3.40 (t, ${}^{3}J = 6.0$ Hz, 8H, CH₂), 3.62, 3.81 (2t, ${}^{3}J = 6.0$ Hz, 8H, E-/Z-CH₂), 6.99 (s, 1H, pz-H⁴), 8.60 (s, 4H, NH). ${}^{13}C{}^{1}H{}$ NMR (D₆-acetone): $\delta = 25.9$ (CH₂), 37.6 (CH₂), 43.9 (CH₂). 46.7 (CH₂), 108.9 (pz-C⁴), 116.9 (q, ${}^{1}J_{CF} = 286$ Hz, CF₃), 143.1 (pz- $C^{3/5}$), 158.0 (q, ² J_{CF} = 30 Hz, COCF₃), 162.9 (CO). ¹⁹F NMR (D₆-acetone): $\delta = -77.3$. MS (FAB+): m/z (%) = 767 (100) [M⁺+1]. The reduction was carried out analogously to the synthesis of H₅L³ to yield H_5L^4 (9.5 g, 15.0 mmol). IR (film): $\tilde{\nu}_{max}/cm^{-1} = 3271(s)$, 2937(s), 2839(s), 1566(w), 1469(w), 1366(w), 1267(s), 1146(s), 952(m), 827(m), 664(m). ¹H NMR (CDCl₃): δ = 1.61 (quint, ${}^{3}J = 6.5$ Hz, 8H, CH₂), 2.45 (t, ${}^{3}J = 6.5$ Hz, 8H, CH₂), 2.70 (t, ${}^{3}J$ = 6.5 Hz, 8H, CH₂), 3.10 (q, ${}^{3}J_{\text{HF}}$ = 9.4 Hz, 8H, CH₂CF₃), 3.54 (s, 4H, CH₂), 5.95 (s, 1H, pz-H⁴). ¹³C{¹H} NMR (CDCl₃): δ = 47.6 (CH₂), 47.8 (CH₂), 49.9 (CH₂), 50.0 (q, ${}^{2}J_{CF}$ = 31 Hz, CH₂CF₃), 51.5 (CH₂), 103.5 (pz-C⁴), 125.2 (q, ${}^{1}J_{CF}$ = 277 Hz, CF₃). ${}^{19}F$ NMR (CDCl₃): $\delta = -72.2$. MS (FAB+): m/z (%) = 683 $(100) [M^++1].$

C25H42N8F12 (682.6)

Calcd C 44.0 H 6.2 N 16.4%, Found C 43.6 H 6.5 N 15.6%.

Ligand H₅L⁵: Starting from pyrazole-3,5-dicarboxylic acid monohydrate (1.3 g, 7.8 mmol) and 1c [15b] (6.7 g, 15.5 mmol) the amide 2c (7.5 g, 7.6 mmol) was prepared as described for 2a. ¹H NMR (D₆-acetone): $\delta = 3.65$ (t, $^{2}J = 5.4$ Hz, 8H, CH₂), 3.65, 3.91 (2t, $^{3}J = 5.4$ Hz, 8H, E-/Z-CH₂), 4.51 (s, 4H, NH), 7.10 (s, 1H, pz-H⁴). ¹³C{¹H} NMR (D₆-acetone): $\delta = 44.6$ (CH₂), 47.8 (CH₂), 49.7 (CH₂), 109.5 (pz-C⁴), 125.1, 130.7, 136.5, 141.0 (m, C_{ar}), 163.1 (CO). ¹⁹F NMR (D₆-acetone): $\delta = -174.0, -168.0,$ -162.0. MS (FAB+) m/z (%) = 991 (16) [M⁺+1], 436 (100) {NH[CH₂CH₂NH(C₆F₅)]₂⁺ + 1}. The reduction of **2c** was carried out under the same conditions as above to yield H_5L^5 (6.0 g, 7.4 mmol, 97 %). IR (film): $\tilde{\nu}_{max}/cm^{-1} =$ 3355 (s), 2941/2842 (vs), 1642 (w), 1606 (s), 1516 (s), 1359 (s), 1275/1183 (vs), 1107 (m), 1037 (s), 814 (m), 784 (m), 627 (m). ¹H NMR (CDCl₃): $\delta = 2.85$ (t, ³J = 5.6 Hz, 8H, CH₂), 3.10 (t, ${}^{3}J$ = 5.6 Hz, 8H, CH₂), 3.72 (s, 4H, CH₂), 5.98 - 6.14 (m, 9H, pz-H⁴ and H_{ar}). ${}^{13}C{}^{1}H$ NMR $(CDCl_3): \delta = 41.4 (CH_2), 50.2 (CH_2), 53.9 (CH_2), 95.8 (m,$ Car), 104.5 (pz-C⁴), 129.8, 135.1, 149.3, 154.1 (m, Car). ¹⁹F NMR (CDCl₃): $\delta = -176.3, -135.1$. MS (FAB+) *m/z* (%) = 819 (55) [M⁺+1], 658 (100) [M⁺-CH₂NHC₆H₂F₃].

C₃₇H₃₃F₁₂N₈ (817.7) Calcd C 54.3 H 4.2 N 13.7%, Found C 53.0 H 4.3 N 12.5%

Ligand H₅L⁶: Starting from pyrazole-3,5-dicarboxylic acid monohydrate (1.2 g, 7.1 mmol) and 1d (6.6 g, 14.2 mmol) the reaction was carried out as described above to yield 2d (6.9 g, 6.7 mmol). ¹H NMR (CDCl₃): $\delta = 1.89$ (quint, ³J = 5.6 Hz, 8H, CH₂), 3.38 (t, ³J = 5.6 Hz, 8H, CH₂), 3.76 (t, ${}^{3}J = 5.6$ Hz, 8H, CH₂), 4.35 (s, 4H, NH), 7.12 (s, 1H, pz-H⁴). ¹³C{¹H} NMR (CDCl₃): $\delta =$ 27.8 (CH₂), 43.1 (CH₂), 43.7 (CH₂), 45.5 (CH₂), 109.6 (pz-C⁴), 123.3, 131.0, 135.4, 140.3 (m, C_{ar}), 161.5 (CO). ¹⁹FNMR (CDCl₃): $\delta = -172.8, -165.2, -160.4$. MS (FAB) $m/z(\%) = 1047 (100) [M^++1], 1027 (40) [M^+-HF], 864$ (88) $[M^+-HNC_6F_5]$, 462 (32) $[{N[(CH_2)_3NHC_6F_5]_2}^+]$. The reduction was carried out analogously to the synthesis of H_5L^3 to yield H_5L^6 (5.5 g, 6.3 mmol, 94 %). IR (film): $\tilde{\nu}_{max}/cm^{-1} = 3265$ (s), 2939/2839 (vs), 1642 (w), 1606 (s), 1517 (s), 1469/1359 (s), 1284/1181 (vs), 1108 (m), 1037 (s), 813 (m), 786 (m), 627 (m). ¹H NMR $(CDCl_3)$: $\delta = 1.85$ (quint, ${}^{3}J = 6.6$ Hz, 8H, CH₂), 2.55 (t, ${}^{3}J = 6.6$ Hz, 8H, CH₂), 3.40 (t, ${}^{3}J = 6.6$ Hz, 8H, CH₂), 6.62 $(s, 4H, CH_2), 6.00 - 6.08 (m, 9H, pz-H^4, H_{ar}).$ ¹³C{¹H} NMR (CDCl₃): $\delta = 25.6$ (CH₂), 42.3 (CH₂), 50.0 (CH₂), 52.0 (CH₂), 95.6 (m, C_{ar}), 104.4 (pz-C⁴), 129.3, 134.0, 149.2, 154.1 (m, C_{ar}). ¹⁹F NMR (CDCl₃): $\delta = -177.0$, -135.0. MS (FAB+) m/z (%) = 875 (40) [M⁺+1], 485 $(100) \{ M^+ - N[(CH_2)_3 NHC_6 H_2 F_3]_2 \}.$

 $C_{41}H_{42}F_{12}N_8$ (874.8)

Calcd C 56.3 H 4.8 N 12.8%, Found C 55.2 H 5.3 N 11.2%.

Ligand H₅L⁷: Na₂CO₃ (1.2 g, 11.4 mmol) was dried by heating to 100 °C under vacuum for 1 h. A solution of the amine 2c (1.0 g, 2.3 mmol) and the tetrahydropyranyl (THP) protected 3,5-bis(chloromethyl)pyrazole 3 [16] (0.3 g, 1.1 mmol) in acetonitrile (50 ml) was added. The mixture was refluxed for 24 h, filtered and the solvent removed under vacuum, yielding the THP-protected ligand as a pale vellow oil. For deprotection ethanolic HCl (50 ml) was added and the mixture stirred for 1 h at room temperature. Addition of diethylether caused the ligand H_5L^7 to precipitate as the hydrochloride salt, which was filtered off and dried under vacuum. Aqueous NaOH was added and extracted two times with 50 ml of CH₂Cl₂. The combined organic phase was dried over MgSO₄. After evaporation of the solvent the ligand H_5L^7 was obtained as a pale yellow oil (0.9 g, 0.9 mmol, 78%). IR (KBr): $\tilde{\nu}_{\text{max}}/\text{cm}^{-1} = 3340$ (s), 2950/2844 (vs), 1656 (s), 1642 (w), 1516 (s), 1349 (s), 1263/1148 (vs), 1099 (s), 1014 (s), 795 (m), 678 (m). ¹H NMR (CDCl₃): $\delta = 2.80$ (t, ³J = 5.5 Hz, 8H, CH₂), 3.39 (t, ${}^{3}J$ = 5.5 Hz, 8H, CH₂), 3.71 (s, 4H, CH₂), 4.25 (s, 4H, NH), 6.10 (s, 1H, pz-H⁴). ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): δ = 43.3 (CH₂), 49.8 (CH₂), 53.6 (CH₂), 103.6 (pz-C⁴), 123.6, 131.0, 135.3, 140.0 (m, C_{ar}). ${}^{19}F{}$ NMR (CDCl₃): δ = -172.3, -164.9, -160.8. MS (FAB+) m/z (%) = 963 (45) [M⁺+1] 766 (100) [M⁺-CH₂NHC₆F₅], 436 (35) {[N(CH₂CH₂NHC₆F₅]]⁺}.

C₃₇H₂₆F₂₀N₈ (962.6)

Calcd C 46.2 H 2.7 N 11.6%, Found C 46.2 H 2.9 N 11.4%.

Ligand H_5L^8 : Starting from 2d (1.3 g, 2.8 mmol) and 3 (4.0 g, 1.4 mmol) the synthesis of H_5L^8 was carried out as described above. Yield (1.1 g, 1.1 mmol, 78%). IR (KBr): $\tilde{\nu}_{max}/cm^{-1} = 3229$ (s), 2947/2858 (vs), 1655 (s), 1642 (w), 1510 (s), 1478/1361 (s), 1262/1148 (vs), 1103 (s), 1060 (m), 1018 (s), 991 (s), 791 (m), 739 (m). ¹H NMR (CDCl₃): $\delta = 1.78$ (quint, ³J = 6.4 Hz, 8H, CH₂), 2.57 (t, ³J = 6.4 Hz, 8H, CH₂), 3.36 (t, ³J = 6.4 Hz, 8H, CH₂), 3.65 (s, 4H, CH₂), 4.33 (s, 4H, NH), 6.07 (s, 1H, pz-H⁴). ¹³C{¹H} NMR (CDCl₃): $\delta = 27.0$ (CH₂), 44.9 (CH₂), 49.9 (CH₂), 51.8 (CH₂), 109.5 (pz-C⁴), 123.6, 130.4, 135.4, 142.2 (m, C_{ar}), 145.5 (pz-C^{3/5}). ¹⁹F NMR (CDCl₃): $\delta =$ -172.8, -165.1, -160.1. MS (FAB+) m/z (%) = 1019 (65) [M⁺+1], 557 (100) {M⁺-N[(CH₂)₃NHC₆F₅]₂}, 464 (75) [{N[(CH₂)₃NHC₆F₅]₂}⁺].

 $C_{41}H_{34}F_{20}N_8$ (1018.7)

Calcd C 48.3 H 3.4 N 11.0%, Found C 48.1 H 3.6 N 10.1%.

Complex L¹Ni₂Cl₃: A solution of HL¹ (0.27 g, 0.52 mmol) in THF (20 ml) was treated with one equivalent of BuLi (2.5 M in hexane). After evaporation to dryness, EtOH (30 ml) and NiCl₂ · 6 H₂O (0.13 g, 1.04 mmol) were added and the reaction mixture stirred at room temperature for 5 d. All volatile material was then removed under vacuum and the residue taken up in CHCl₃ (30 ml) and filtered. The volume of the resulting green solution was reduced to ~ 15 ml and layered with light petroleum to gradually afford green crystals of L¹Ni₂Cl₃·2CHCl₃ (0.25 g, 0.25 mmol, 49%). The solvent molecules are lost upon storage in air. MS (FAB+, nibeol): m/z (%) = 709 (100) [L¹Ni₂Cl₂⁺], 672 (40) [L¹Ni₂Cl⁺]. IR (KBr pellet): $\tilde{\nu}_{max}/cm^{-1}$ = 2966 (m), 1467 (s), 1382 (m), 1097 (s), 1054 (s).

 $\begin{array}{c} C_{29}H_{61}Cl_3N_8Ni_2\ (745.6)\\ Calcd \ C\ 46.7\ H\ 8.3\ N\ 15.0\%,\\ Found \ C\ 45.7\ H\ 7.9\ N\ 14.8\%. \end{array}$

Complex L²Ni₂Cl₃: This compound was prepared in close analogy to the preparation of L¹Ni₂Cl₃, but starting from HL² (0.23 g, 0.49 mmol) to afford green crystals of L²Ni₂Cl₃ (0.25 g, 0.25 mmol, 49%). MS (FAB+, nibeol): m/z (%) = 653 (100) [L²Ni₂Cl₂⁺]. IR (KBr pellet): $\tilde{\nu}_{max}/cm^{-1}$ = 2922 (m), 1472 (s), 1306 (m).

	L ¹ Ni ₂ Cl ₃	L ² Ni ₂ Cl ₃	H ₄ L ⁴ Ni ₂ Cl ₃	$H_4L^4Co_2Cl_3\\$	H ₅ L ⁴ Co ₂ Cl ₄
Formula	C ₂₉ H ₆₁ Cl ₃ N ₈ Ni ₂ · 2 CHCl ₃	C ₂₅ H ₅₃ Cl ₃ N ₈ Ni ₂	$\begin{array}{c} C_{25}H_{41}Cl_{3}F_{12}N_{8}Ni_{2}\\ \cdot \ 0.75CH_{2}Cl_{2} \end{array}$	$\begin{array}{c} C_{25}H_{41}Cl_3F_{12}N_8Ni_2O\\ \cdot CHCl_3 \end{array}$	C ₂₅ H ₄₂ Cl ₄ - C ₀₂ F ₁₂ N ₈
$M_{\rm r}$	745.6	689.5	905.4	905.9	942.3
Crystal size [mm]	$0.25 \times 0.20 \times 0.30$	$0.40 \times 0.30 \times 0.20$	$0.15 \times 0.15 \times 0.10$	$0.20 \times 0.10 \times 0.15$	0.20×0.20×0.20
Crystal system	monoclinic	tetragonal	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	P43212	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a[Å]	12.33(2)	9.338(1)	11.629(2)	11.697(2)	9.407(2)
<i>b</i> [Å]	21.29(1)	9.338(1)	12.139(2)	12.269(3)	11.515(1)
c [Å]	17.30(1)	37.527(3)	27.496(6)	27.481(6)	17.692(2)
α [°]	90	90	90	90	87.13(1)
β [°]	90.36(7)	90	98.25(3)	97.69(3)	79.77(1)
γ [°]	90	90	90	90	85.96(1)
$V[Å^3]$	4543(1)	3272(1)	3841(1)	6908(1)	1880(1)
$\rho_{\text{calcd.}} [\text{g cm}^{-3}]$	1.439	1.400	1.676	1.741	1.665
Z	4	4	4	4	2
F(000) [e]	2056	1464	1974	2072	956
<i>T</i> [K]	200	200	200	200	200
μ (Mo-K _{α}) [mm ⁻¹]	1.39	1.42	1.38	1.35	1.258
hkl Range	±14, -7 - 25, ±19	0 - 11, 0 - 11, 0 - 46	$\pm 14, \pm 14, \pm 33$	$\pm 14, \pm 15, \pm 33$	$0 - 10, \pm 13, \pm 21$
2θ Range [°]	2.4 - 49.9	4.3 - 52.0	3.0 - 52.0	3.0 - 52.0	4.2 - 50.0
Measured refl.	7703	3665	58284	59867	6513
Unique refl. (Rint)	7095 (0.042)	3227 (0.028)	7481 (0.109)	7699 (0.078)	6061 (0.020)
Observed refl. I > $2\sigma(I)$	5527	2747	5140	6045	4652
Refined parameters	479	182	484	502	484
Resididual electron density $[eÅ^{-3}]$	0.97/-0.76	0.26/-0.35	0.79/-0.48	0.37/-0.52	0.89/-0.85
R1	0.061	0.033	0.047	0.036	0.039
wR2 (refinement on F ²)	0.164	0.083	0.109	0.081	0.079
Goodness-of-fit	1.082	1.355	1.044	1.034	1.210

Table VII. Crystal data and refinement details.

C₂₅H₅₃Cl₃N₈Ni₂ (689.5)

Calcd C 43.6 H 7.8 N 16.3%, Found C 43.2 H 7.8 N 15.1%.

Complex H₄L⁴Ni₂Cl₃: A solution of H₅L⁴ (0.21 g,

0.30 mmol) in THF (50 ml) was treated with an excess of triethylamine (0.21 g, 2.01 mmol) and NiCl₂·6H₂O (0.15 g, 0.60 mmol) was added. The resulting green suspension was stirred at room temperature for 12 h. Then the inorganic salts were filtered off and the resulting green solution was evaporated to dryness to yield a green powder. Green crystals (0.22 g, 0.23 mmol, 75%) were obtained by layering a solution of the complex in CH₂Cl₂ with diethylether. MS (FAB+, nibeol): m/z (%) = 869 (100) [H₄L⁴Ni₂Cl₂⁺]. IR (KBr pellet) $\tilde{\nu}_{max}/cm^{-1}$ = 3437 (m), 3293 (m), 3183 (m), 2937 (s), 2733 (m), 2671 (m), 2598 (m), 2489 (m), 1622 (w), 1468 (m), 1379 (m), 1263 (s), 1157 (s), 1102 (s), 1035 (m), 986 (m), 905 (m), 865 (w), 680 (m).

 $C_{25}H_{41}Cl_3F_{12}N_8Ni_2 \cdot 0.75 CH_2Cl_2$ (969.1)

Calcd C 31.9 H 4.4 Cl 16.5 N 11.7%,

Found C 31.5 H 4.5 Cl 17.5 N 11.3%.

Complex H₄L⁴Co₂Cl₃: Starting from H_5L^4 (0.35 g, 0.52 mmol), CoCl₂·6H₂O (0.25 g, 1.04 mmol) and an

excess of triethylamine (0.52 g, 5.20 mmol) the preparation was carried out analogously to that for H₄L⁴Ni₂Cl₃ to yield a blue powder. Layering a solution of the crude complex in CHCl₃ with diethylether affords dark blue crystals (0.38 g, 0.39 mmol, 71%). MS (FAB+, nibeol): m/z (%) = 869 (100) [H₄L⁴Co₂Cl₂⁺]. IR (KBr pellet): $\tilde{\nu}_{max}/cm^{-1}$ = 3441 (m), 2953 (m), 1624 (m), 1461 (m), 1379 (m), 1263 (s), 1157 (s), 1102 (s), 1038 (s), 973 (w), 901 (w), 823 (w), 678 (m).

 $\begin{array}{c} C_{25}H_{41}Cl_3F_{12}N_8Co_2\cdot 0.5 \ CHCl_3 \ (1025.2) \\ Calcd \ C \ 31.7 \ H \ 4.3 \ Cl \ 16.5 \ N \ 11.6\%, \\ Found \ C \ 32.1 \ H \ 4.8 \ Cl \ 16.2 \ N \ 11.7\%. \end{array}$

Complex H₅L⁴Ni₂Cl₄: A solution of H₅L⁴ (0.70 g, 1.03 mmol) in THF (50 ml) was treated with two equivalents of NiCl₂·6H₂O (0.49 g, 2.06 mmol) and stirred at room temperature for 12 h. The resulting green solution was evaporated to dryness to yield a green powder which was washed with diethylether to remove unreacted organic compounds and finally dried under vacuum. Green crystals (0.66 g, 68%) could be obtained by layering a solution of the complex in CH₂Cl₂ with diethylether. MS (FAB+, nibeol): m/z (%) = 867 (100) [H₄L⁴Ni₂Cl₂⁺]. IR (KBr pellet): $\tilde{\nu}_{max}/cm^{-1}$ = 3213 (m), 3193 (m), 2957 (m),

1620 (m), 1554 (m), 1468 (m), 1382 (m), 1337 (w), 1266 (s), 1156 (s), 1098 (s), 1039 (m), 975 (m), 905 (m), 824 (w), 681 (m).

C₂₅H₄₂Cl₄F₁₂N₈Ni₂ (941.8)

Calcd C 31.9 H 4.5 Cl 15.1 N 11.9%.

Found C 32.6 H 5.0 Cl 14.7 N 11.7%.

Complex H₅L⁴Co₂Cl₄: Starting from H₅L⁴ (0.35 g, 0.52 mmol) and CoCl₂·6H₂O (0.25 g, 1.03 mmol) the preparation was carried out analogously to that of H₅L⁴Ni₂Cl₃ to yield a blue powder. Layering a solution of the crude complex in CH₂Cl₂ with diethylether afforded dark blue crystals (0.45 g, 91%). MS (FAB+, nibeol): m/z (%) = 869 (100) [H₄L⁴Co₂Cl₂⁺]. IR (KBr pellet): $\tilde{\nu}_{\text{max}}/\text{cm}^{-1} = 3438 \text{ (m)}, 3293 \text{ (m)}, 2957 \text{ (m)}, 1620 \text{ (m)},$ 1460 (m), 1379 (m), 1262 (s), 1152 (s), 1100 (s), 1040 (s), 976 (m), 901 (m), 823 (w), 678 (m).

C25H42Cl4F12N8C02 (942.3)

Calcd C 31.9 H 4.5 Cl 15.1 N 11.9%, Found C 31.8 H 4.8 Cl 15.8 N 11.8%.

X-ray crystallography

The measurements were carried out on a Nonius Kappa CCD diffractometer [complexes H₄L⁴Ni₂Cl₃, H₄L⁴Co₂Cl₃, and H₅L⁴Ni₂Cl₄] or a Siemens P4 fourcircle diffractometer [complexes L¹Ni₂Cl₃, L²Ni₂Cl₃, and $H_5L^4Co_2Cl_4$ using graphite-monochromated Mo- K_{α} radiation. For the latter three complexes the intensities of three check reflections (measured every 100 reflections) remained constant throughout the data collection (thus indicating crystal and electronic stability) and an absorption correction (ψ scan, $\Delta \psi = 10^{\circ}$) was applied to the data. All calculations were performed using the SHELXT PLUS software package. Structures were solved by direct methods with the SHELXS-93 [complexes L¹Ni₂Cl₃ and

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 $H_4L^4Co_2Cl_3$, $H_5L^3Ni_2Cl_4$, $H_5L^4Ni_2Cl_4$ and $H_5L^4Co_2Cl_4$] and refined with the SHELXL-93 or SHELXL-97 program, respectively [23]. In the case of L¹Ni₂Cl₃ a twinned crystal had been examined and was refined using the TWIN routine (BASF 0.30844). Atomic coordinates and thermal parameters of the non-hydrogen atoms were refined in fully or partially anisotropic models by fullmatrix least-squares calculation based on F². In general the hydrogen atoms were placed at calculated positions and allowed to ride on the atoms they are attached to. In the cases of H₄L⁴Co₂Cl₃ and H₅L⁴Co₂Cl₄ the N-bound protons could be located in the difference Fourier synthesis and refined. In Table VII the data for the structure determinations are compiled. Crystallographic data (excluding structure factors) for the structures reported in this paper (except for $H_5L^4Ni_2Cl_4$ [21]) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 114054, 114055, 114057, and 114059. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk].

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