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Coordination Compounds of the Chelating Tridentate Pyrazole-Containing Ligand Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (ddaH). Crystal and Molecular Structures of $[Cu(ddaH)Cl]_2(CuCl_4)$, $[Co(ddaH)Cl]_2(CoCl_4)$, $[Cu(ddaH)Cl](BF_4)$, and $[Co(ddaH)Cl](BF_4)$

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The synthesis, spectroscopy, and structure of transition-metal coordination compounds of the ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (abbreviated ddaH) are described. The ligand acts as a tridentate N_3-donor ligand in the compounds $[M(ddaH)Cl]_2(MCl_4)$ with $M = Cu^{2+}$, Co^{2+}, and Zn^{2+}, and in the compounds $[M(ddaH)Cl](BF_4)$ with $M = Cu^{2+}$ and Co^{2+}, as shown spectroscopically and—in a selected number of cases—proven by X-ray diffraction. The compound $[Cu(ddaH)Cl]_2(CuCl_4)$ crystallizes in the monoclinic space group *C2/c* ($Z = 4$). The cell dimensions are $a = 23.207(9)$ Å, $b = 11.614(5)$ Å, $c = 14.408(4)$ Å, $\beta = 90.26(4)°$, $V = 3883(2)$ Å^3, $D_x = 1.584$ g/cm^3, and $R = 0.056$ ($R_w = 0.058$) for 1765 significant reflections. The copper(II) ion in the cationic part is surrounded by two pyrazole nitrogens (Cu−N distances are 1.999(8) and 1.980(7) Å) and an amine nitrogen (Cu−N distance is 2.022(7) Å) from the ligand and by one chloride anion (Cu−Cl distance is 2.232(3) Å) in a distorted tetrahedral coordination geometry. The compound $[Co(ddaH)Cl]_2(CoCl_4)$ crystallizes in the monoclinic space group *C2/c* (Z = 4). The cell dimensions are $a = 20.810(7)$ Å, $b = 13.429(3)$ Å, $c = 14.284(2)$ Å, $\beta = 92.53(2)°$, $V = 3988(2)$ Å^3, $D_x = 1.519$ g/cm^3, and $R = 0.040$ ($R_w = 0.052$) for 2825 significant reflections. The cobalt(II) ion in the cationic part is surrounded by two pyrazole nitrogens (Co−N distances are 2.004(3) and 1.982(3) Å) and an amine nitrogen (Co−N distance is 2.068(3) Å) from the ligand and by one chloride anion (Co−Cl distance is 2.216(1) Å) in a distorted tetrahedral coordination geometry. The anionic part of both compounds consists of a distorted tetrahedral tetrachlorometalate(II) with a Cu−Cl distance of 2.215−2.282 Å, a Co−Cl distance of 2.255−2.289 Å, a Cl−Cu−Cl bond angle of 100.8−137.0°, and a Cl−Co−Cl bond angle of 104.1−116.4°. There is a moderately strong hydrogen bridge between the $(MCl_4)^{2-}$ anion and the amine nitrogen of the ligand ddaH. The shortest distances from the $(MCl_4)^{2-}$ anion to the M^{2+} in the cation are 4.26 Å and 3.673 Å for respectively Co^{2+} and Cu^{2+}. The compound $[Cu(ddaH)Cl](BF_4)$ crystallizes in the orthorombic space group *Pbca* ($Z = 8$). The cell dimensions are $a = 10.163(2)$ Å, $b = 19.542(3)$ Å, $c = 19.647(3)$ Å, V = 3898(2) Å^3, $D_x = 1.524$ g/cm^3, and $R = 0.056$ ($R_w = 0.032$) for 1134 significant reflections. The Cu^{2+} ion in $[Cu(ddaH)Cl]^+$ is surrounded by two pyrazole nitrogens (Cu−N distances are 1.977(8) and 1.962(9) Å) and an amine nitrogen (Cu−N distance is 2.038(9) Å) from the ligand and by one chloride anion (Cu−Cl distance is 2.247(3) Å) in a distorted tetrahedral coordination geometry. The compound $[Co(ddaH)Cl](BF_4)$ crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$). The cell dimensions are $a = 12.372(1)$ Å, $b = 14.297(1)$ Å, $c = 12.753(1)$, $\beta = 117.55(1)°$, $V = 2000(1)$ Å^3, $D_x = 1.470$ g/cm^3, and $R = 0.046$ ($R_w = 0.035$) for 2198 significant reflections. The Co^{2+} ion in $[Co(ddaH)Cl]^+$ is surrounded by two pyrazole nitrogens (Co−N distances are 1.977(3) and 1.985(5) Å) and an amine nitrogen (Co−N distance is 2.057(5) Å) from the ligand and by one chloride anion (Cu−Cl distance is 2.207(2) Å) in a distorted tetrahedral coordination geometry. In all compounds, the tetrafluoroborate anions are weakly hydrogen bridged to the amine nitrogen of the ligand. The compound $[Zn(ddaH)Cl]_2(ZnCl_4)$ is IR isomorphous with the corresponding copper(II) and cobalt(II) compounds.

Introduction

A unique feature of metalloproteins is their ability to discriminate between various metal ions which are present in their natural surroundings. The active site of a metalloprotein is build up in such a way that only a few specific metal ions fit in, making the metal ions an integral part of the active site. In proteins like plastocyanin, azurin, and haemocyanin only copper ions are present in the active site. The architecture of the active site determines the specific function of the different copper proteins.[1−3] Synthesis of model compounds for the active sites can provide better insight into the relation between the structure and activity of the active sites of these proteins.

Synthetic analogs can be anchored onto a solid support, and in this way systems with a high selectivity for one specific metal ion and/or catalytic activity can be obtained.[4−6] The ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine (ddaH) (see Figure 1), synthesized earlier by Sorrell and Malachowski,[7] was immobilized onto the organic polymer poly(glycidyl methacrylate-

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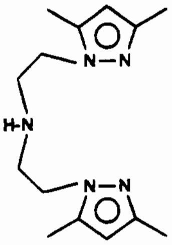

Figure 1. Schematic drawing of the ligand ddaH.

co-ethylene glycol dimethacrylate) by reaction of the secondary amine with the epoxy group of the polymer.[8,9] The resulting resin has been tested for its metal binding properties, and a strong preference for Cu(II) was found.[10]

Usually relatively little information can be obtained about the coordination environment of such metal ion complexes in the heterogeneous phase; therefore, some relevant coordination compounds with the ligand ddaH were prepared in the homogeneous phase. Besides a copper(I) tetrafluoroborate compound,[7] only two other coordination compounds with this ligand have recently been reported, *i.e* a copper(II) nitrate and a copper(II) perchlorate.[11] X-ray structure determinations were only performed on the latter two Cu(II) compounds. In the present paper copper(II), cobalt(II), and zinc(II) complexes with the ligand ddaH and chloride and/or tetrafluoroborate as the anion are presented and discussed in their relationships to chelation on an ion-exchange resin. Crystal structure determinations were performed of the copper(II) and the cobalt(II) compounds with chloride as the anion, and with the mixed-anion compounds, *i.e* chloride and tetrafluoroborate as the anions. The complexes have further been characterized by infrared, ligand field, and EPR spectroscopy.

Experimental Section

Starting Materials and Syntheses. All chemicals were commercially available, of sufficient purity, and were used without further treatment. The synthesis of the ligand bis(2-[3,5-dimethyl-1-pyrazolyl]-ethyl)amine (ddaH) has been described elsewhere.[7]

The coordination compounds [M(ddaH)Cl]$_2$(MCl$_4$) were prepared by dissolving the appropriate hydrated metal salt (2 mmol) in 15 mL of hot ethanol, followed by adding 4 mL of triethyl orthoformate for dehydration. To this solution, a solution of the ligand ddaH (2 mmol) in 10 mL of hot ethanol was added. For the preparation of the mixed-anion coordination compounds [M(ddaH)Cl](BF$_4$) a combination of the appropriate hydrated metal salts was used. Two millimoles of each metal salt was dissolved in 20 mL of hot ethanol, followed by addition of 8 mL of triethyl orthoformate for dehydration. A solution of the ligand ddaH (4 mmol) in 15 mL of hot ethanol was studied. After filtration of the reaction mixture, the complexes crystallized on cooling. The crystals were filtered and washed with ethanol.

Metal analyses were carried out complexometrically with H$_4$edta as the complexing agent[12] after destruction of the samples by heating them with concentrated sulfuric acid and nitric acid. Chloride contents were determined by potentiometric titrations with AgNO$_3$ as the precipitating agent.[13] Other elements (C, H, N, F) were analysed at the Mikroanalytisches Labor Pascher, Remagen, Germany, and at the Microanalytical Laboratory of the Groningen University, Groningen, The Netherlands.

Infrared spectra of the compounds pressed in KBr pellets or in a CHCl$_3$ solution between KBr discs, were recorded in the 4000−180 cm^{-1} range on a Perkin-Elmer spectrophotometer, equipped with a PE data station.

Solid state electronic spectra (28000−5000 cm^{-1}), using the diffuse reflectance method with MgO as reference, were recorded on a Perkin-Elmer 330 spectrophotometer, equipped with a PE data station.

Electron paramagnetic resonance spectra of the powdered copper(II) complexes were recorded on a Jeol RE2x spectrometer at X-band frequency at liquid-nitrogen temperature.

Data Collection and Structure Refinement of [Cu(ddaH)Cl]$_2$(CuCl$_4$) and [Co(ddaH)Cl]$_2$(CoCl$_4$). This was carried out at room temperature on a Nicolet P3 diffractometer using graphite-monochromatized Mo Kα radiation (λ(Mo Kα) = 0.710 69 Å) and ω-scan mode. Accurate unit-cell parameters were obtained by least-squares fit of 25 reflections (7° < 2θ < 25°). Crystal data and additional details of the data collection and refinement for the two structures are presented in Table 1. Intensity data were corrected for Lorentz and polarization effects and absorption from empirical ϕ-scan data. The structures were solved by direct and Fourier methods of the SHELXTL-Plus program[14] and refined with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions and refinement with fixed geometry with respect to their carrier atoms. For the Co(II) compound final $R = 0.040$, $R_w = 0.052$, and $S = 1.51$ for 213 variables, with weighting scheme $w^{-1} = \sigma^2(R) + 0.0005F^2$. Maximum and minimum heights in final difference Fourier synthesis were +0.77 and −0.53 e Å^{-3} and largest $\Delta/\sigma = 0.23$. For the Cu(II) compound final $R = 0.056$, $R_w = 0.058$, and $S = 1.44$ for 213 variables, with weighting scheme $w^{-1} = \sigma^2(F) + 0.0005F^2$. Maximum and minimum heights in final difference Fourier synthesis were +0.95 and −0.57 e Å^{-3} and largest $\Delta/\sigma = 0.10$. The fractional coordinates and the equivalent isotropic displacement coefficients of the non-hydrogen atoms of both compounds are listed in Table 2a,b. Selected bond distances and selected bond angles are given in Table 3a,b. See also the supplementary material.

Data Collection and Structure Refinement of [Cu(ddaH)Cl](BF$_4$) and [Co(ddaH)Cl](BF$_4$). This was carried out at room temperature on a Rigaku AFC7 diffractometer using graphite-monochromated Mo Kα radiation (λ(Mo Kα) = 0.710 73 Å) and 2θ/ω-scan mode. Accurate unit-cell parameters were obtained by least-squares fit of 25 reflections (25° < 2θ < 35°). Crystal data and additional details of the data collection and refinement for the two structures are presented in Table 1. Intensity data were corrected for Lorentz and polarization effects and absorption from empirical ϕ-scan data. The structures were solved by direct and Fourier methods of the SHELXTL-Plus program[14] and refined with anisotropic temperature factors for non-hydrogen atoms (except for the BF$_4^-$ group in the [Co(ddaH)Cl](BF$_4$) compound which had a population parameter of 0.25). Hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. For the Co(II) compound the BF$_4^-$ group was disordered and was refined as a rigid group in two positions. For the Cu(II) compound final $R = 0.056$, $R_w = 0.032$, $S = 1.91$ for 140 variables, with a weighing scheme $w^{-1} = \sigma^2$(F). Maximum and minimum heights in final difference Fourier synthesis were +0.44 and −0.50 e Å^{-3} and largest $\Delta/\sigma = 0.004$. For the Co(II) compound final $R = 0.046$, $R_w = 0.035$, and $S = 2.34$ for 235 variables, with weighing scheme $w^{-1} = \sigma^2$(F). Maximum and minimum heights in final difference Fourier synthesis were +0.36 and −0.31 e Å^{-3} and largest $\Delta/\sigma = 0.13$. The fractional coordinates and the equivalent isotropic displacement coefficients of the non-hydrogen atoms of both compounds are listed in Table 2c,d. Selected bond distances and selected bond angles are given in Table 3c,d. See also the supplementary material.

Results and Discussion

General Data. A listing of colors, spectroscopic data (ligand field and EPR) and characterization data of the complexes with

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Table 1. Crystal and Refinement Data for the Compounds [Cu(ddaH)Cl]$_2$(CuCl$_4$) (**A**), [Co(ddaH)Cl]$_2$(CoCl$_4$) (**B**), [Cu(ddaH)Cl](BF$_4$) (**C**) and [Co(ddaH)Cl](BF$_4$) (**D**)

	A	B	C	D
formula	$C_{28}H_{46}Cl_6Cu_3N_{10}$	$C_{28}H_{46}Cl_6Co_3N_{10}$	$C_{14}H_{23}BClCuF_4N_5$	$C_{14}H_{23}BClCoF_4N_5$
fw	926.1	912.2	447.2	442.6
a (Å)	23.207(9)	20.810(7)	10.163(2)	12.372(1)
b (Å)	11.614(5)	13.429(3)	19.524(3)	14.297(1)
c (Å)	14.408(4)	14.284(2)	19.647(3)	12.753(1)
β (deg)	90.26(4)	92.53(2)		117.55(1)
V (Å^3)	3883(2)	3988(2)	3898(2)	2000(1)
T (K)	296	296	296	296
F(000)	1892	1868	1832	908
cryst syst	monoclinic	monoclinic	orthorombic	monoclinic
space group	$C2/c$	$C2/c$	$Pbca$	$P2_1/c$
Z	4	4	8	4
D_x (g/cm^3)	1.584	1.519	1.524	1.470
μ (cm^{-1})	20.76	16.70	13.0	10.4
cryst dimens	0.10 × 0.15 × 0.25	0.25 × 0.30 × 0.30	0.10 × 0.10 × 0.15	0.30 × 0.30 × 0.30
color	green	blue	green	blue
h-values	0 to 29	0 to 26	0 to 12	0 to 15
k-values	0 to 14	0 to 16	0 to 24	0 to 17
l-values	−18 to +18	−17 to +17	0 to 24	−15 to +14
scan range, 2θ (deg)	3.0−53.0	4.0−53.0	3.0−53.0	3.0−53.0
no. of unique reflcns	4036	4042	2988	3585
no. used in refinement	1765	2825	1134	2198
no. of params	213	213	140	235
excursions: max; min (e/Å^3)	0.95; −0.57	0.77; −0.53	0.44; −0.50	0.36; −0.31

copper(II), cobalt(II), and zinc(II) is presented in Table 4. The elemental analyses are in good agreement with the formulations; see the supplementary material. In the cationic part all compounds have a metal-to-ligand ratio of 1:1. Experiments designed to obtain M:L = 1:2 compounds using excess of ligand resulted solely in the formation of 1:1 compounds. A PLUTON[15] projection of the cationic part ([M(ddaH)Cl]$^+$) of the four compounds is given in Figure 2, together with the atomic labelling scheme. The four structures are so much alike, that projections of the four structures can in fact hardly be distinguished from each other, therefore only one projection is shown in which M1 represents Cu(1) or Co(1). For clarity the (MCl$_4$)$^{2-}$ anion and the BF$_4$$^-$ anion are omitted. The differences between the four cations are relatively small, and will be discussed below in more detail.

Description of the Crystal Structure of [Co(ddaH)Cl]$_2$(CoCl$_4$). The asymmetric unit consists of one molecule of [Co(ddaH)Cl]$^+$ and half a molecule of the tetrachlorocobaltate(II) anion. The cobalt(II) atom in the [Co(ddaH)Cl]$^+$ cation is surrounded by two pyrazole nitrogens and an amine nitrogen from the ligand and one chloride anion. Relevant bond distances and angles are given in Table 3b. The nitrogen−cobalt distances are 2.00 and 1.98 Å for the pyrazole nitrogens and 2.07 Å for the amine nitrogen. The Cl−Co distance in the cation is 2.22 Å. From the bond distances and angles it can be concluded that the coordination geometry around the cobalt(II) atom in [Co(ddaH)Cl]$^+$ can be described as distorted tetrahedral. In the tetrachlorocobaltate(II) anion there is also a distorted tetrahedral coordination environment around the cobalt(II) atom present. The shortest distance from a (CoCl$_4$)$^{2-}$ anion to the Co^{2+} ion in the cation is 4.26 Å. The N(10)−Cl(2) distance is 3.365 Å, which indicates that there is a moderate strong hydrogen-bridge interaction between the cation and the (CoCl$_4$)$^{2-}$ anion. The molecules are further packed according to normal van der Waals forces and there is no intermolecular stacking of the pyrazole rings.

Description of the Crystal Structure of [Cu(ddaH)Cl$_2$(CuCl$_4$). The asymmetric unit consists of one molecule of [Cu(ddaH)Cl]$^+$ and half a molecule of the tetrachlorocuprate(II) anion. The coordination environment of the copper(II) atom in the [Cu(ddaH)Cl]$^+$ cation is made up by two pyrazole nitrogens with copper-nitrogen distances of 2.00 and 1.98 Å and one amine nitrogen with a copper-nitrogen distance of 2.02 Å. The chloride-copper distance in the cation is 2.23 Å. Other relevant bond distances are given in Table 3a. From the bond distances and angles it can be concluded that the coordination geometry around the copper(II) atom in [Cu(ddaH)Cl]$^+$ can be described as distorted tetrahedral, where the distortion is towards square planar although the largest angle (N(12)−Cu(1)−N(22) of 141°) is still far from the 180° for a square. Also the (CuCl$_4$)$^{2-}$ anion is slightly distorted from tetrahedral as indicated by the two different Cu−Cl distances and the deviation from the tetrahedral angles (see Table 3a). The shortest contact between the (CuCl$_4$)$^{2-}$ anion and the Cu^{2+} ion in the cation is 3.673 Å (Cu(1)−Cl(3)). The N(10)−Cl(3) distance is 3.255 Å, indicating that there is a moderately strong hydrogen-bridge interaction present between the cation and the tetrachlorocuprate(II) anion. The packing of the molecules is further dictated by normal van der Waals contacts and there is no intermolecular stacking of the pyrazole rings.

Description of the Crystal Structure of [Cu(ddaH)Cl](BF$_4$). The asymmetric unit consists of one molecule of [Cu(ddaH)Cl]$^+$ and one non-coordinating tetrafluoroborate anion. The copper(II) atom is coordinated by two pyrazole nitrogens with copper−nitrogen distances of 1.98 and 1.96 Å and one amine nitrogen with a copper−nitrogen distance of 2.04 Å. The chloride−copper distance is 2.25 Å. Other relevant bond distances and angles are given in Table 3c. The coordination geometry around the copper(II) atom can again be described as square planar distorted tetrahedral, with the largest angle N(12)−Cu(1)−N(22) now being 155°. No other potential ligands are within semi-coordination distance of Cu(II), as deduced from the Cu(1)−F(2) distance of 5.70(7) Å. The tetrafluoroborate anion is not disordered and shows a weak hydrogen-bridge interaction, N(10)−F(2) = 3.03(6) Å. The packing of the molecules is furthermore dictated by normal van der Waals forces and there is no intermolecular stacking of the pyrazole rings.

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Table 2. Fractional Coordinates (×10⁴) and Isotropic Temperature Factors (Å² × 10³) of Non-Hydrogen Atoms

atom	*x*	*y*	*z*	*U*(eq)[a]	atom	*x*	*y*	*z*	*U*(eq)[a]
a. $[Cu(ddaH)Cl]_2(CuCl_4)$ (**A**)									
Cu(1)	3329(1)	1561(1)	6710(1)	39(1)	C(15)	4719(4)	3760(9)	6324(6)	49(4)
Cu(2)	5000	8476(2)	7500	57(1)	C(16)	3299(4)	4467(9)	7235(6)	60(4)
Cl(1)	2984(1)	1755(2)	8145(2)	56(1)	C(17)	5324(4)	3891(10)	5996(7)	66(4)
Cl(2)	4665(2)	7777(3)	6173(2)	97(1)	C(18)	4695(4)	1619(9)	6172(6)	53(4)
Cl(3)	5781(1)	9490(3)	6996(2)	72(1)	C(19)	4333(4)	910(8)	5514(7)	49(4)
N(10)	3811(3)	434(6)	5978(5)	37(3)	C(23)	2104(4)	1678(9)	5976(6)	43(3)
N(11)	4455(3)	2729(7)	6360(5)	40(3)	C(24)	1720(4)	986(9)	5481(6)	45(3)
N(12)	3905(3)	2842(7)	6696(5)	40(3)	C(25)	1978(4)	−47(9)	5341(6)	43(3)
N(21)	2509(3)	309(6)	5725(5)	39(3)	C(26)	2048(4)	2872(9)	6308(7)	62(4)
N(22)	2600(3)	1074(6)	6110(5)	38(3)	C(27)	1763(4)	−1134(8)	4896(6)	51(4)
C(13)	3843(4)	3962(10)	6864(6)	45(4)	C(28)	2970(4)	−839(8)	5746(7)	45(3)
C(14)	4331(4)	4557(9)	6640(6)	53(4)	C(29)	3517(3)	−377(8)	5332(6)	43(3)
b. $[Co(ddaH)Cl]_2(CoCl)_4$ (**B**)									
Co(1)	3489(1)	1628(1)	6909(1)	35(1)	C(15)	2200(2)	−120(3)	5344(3)	45(1)
Co(2)	5000	1946(1)	2500	42(1)	C(16)	1968(3)	2386(4)	6308(5)	88(3)
Cl(1)	3483(1)	1688(1)	8459(1)	60(1)	C(17)	2076(2)	−1094(4)	4870(4)	65(2)
Cl(2)	4340(1)	898(1)	3279(1)	46(1)	C(18)	3326(2)	−551(3)	5987(3)	44(1)
Cl(3)	5630(1)	2832(1)	3520(1)	81(1)	C(19)	3945(2)	−61(3)	5725(3)	41(1)
N(10)	4187(1)	672(2)	6447(2)	33(1)	C(23)	3769(2)	3860(3)	6839(3)	44(1)
N(11)	2762(2)	88(3)	5821(2)	40(1)	C(24)	4305(2)	4429(3)	6654(3)	51(2)
N(12)	2741(2)	1012(3)	6222(2)	42(1)	C(25)	4712(2)	3836(3)	6164(3)	41(1)
N(21)	4422(2)	2940(2)	6064(2)	38(1)	C(26)	3186(2)	4151(4)	7331(3)	61(2)
N(22)	3836(2)	2937(2)	6486(2)	40(1)	C(27)	5360(2)	4054(4)	5806(3)	58(2)
C(13)	2154(2)	1383(3)	5982(3)	50(2)	C(28)	4626(2)	2080(3)	5533(3)	42(1)
C(14)	1815(2)	698(4)	5442(3)	52(2)	C(29)	4777(2)	1183(3)	6139(3)	42(1)
c. $[Cu(ddaH)Cl](BF_4)$ (**C**)									
Cu(1)	293(1)	4229(1)	2192(1)	43(1)	N(22)	910(9)	4786(5)	1425(4)	43(3)
Cl(1)	−1790(3)	4613(2)	2174(2)	56(1)	C(23)	1097(12)	5462(6)	1364(6)	49(4)
N(10)	1095(9)	3342(4)	1836(4)	48(3)	C(24)	1531(11)	5639(6)	720(6)	53(4)
N(11)	480(10)	3277(5)	3375(4)	48(3)	C(25)	1639(11)	5048(6)	374(6)	47(4)
N(12)	250(10)	3927(4)	3153(4)	40(2)	C(26)	837(11)	5918(6)	1960(5)	81(5)
C(13)	86(11)	4330(5)	3720(5)	43(3)	C(27)	2028(11)	4902(6)	−349(6)	69(5)
C(14)	169(12)	3900(5)	4272(5)	50(3)	C(28)	1227(11)	3791(6)	670(6)	55(4)
C(15)	391(14)	3264(7)	4064(6)	59(4)	C(29)	1914(11)	3397(5)	1232(5)	48(4)
C(16)	−173(11)	5070(5)	3665(5)	50(3)	B(1)	−1092(25)	1996(11)	1160(10)	80(10)
C(17)	581(13)	2595(6)	4443(6)	93(5)	F(1)	−1728(11)	1768(5)	1712(5)	160(6)
C(18)	728(11)	2722(5)	2906(6)	56(4)	F(2)	−1232(9)	2675(4)	1128(5)	113(5)
C(19)	1693(10)	2902(5)	2351(5)	50(4)	F(3)	222(10)	1842(5)	1237(5)	127(5)
N(21)	1263(9)	4521(5)	793(4)	42(3)	F(4)	−1516(9)	1673(5)	640(4)	128(5)
d. $[Co(ddaH)Cl](BF_4)$ (**D**)									
Co(1)	7759(1)	8794(1)	1692(1)	47(1)	C(25)	8313(5)	10655(4)	4371(5)	61(3)
Cl(1)	8390(1)	7341(1)	2190(1)	76(1)	C(26)	6633(5)	8446(4)	3696(5)	82(4)
N(10)	9034(3)	9567(3)	1460(3)	52(2)	C(27)	8931(6)	11541(4)	4983(4)	96(4)
N(11)	6645(4)	9065(3)	−892(4)	52(2)	C(28)	8807(5)	10850(4)	2660(5)	72(3)
N(12)	6427(3)	8882(3)	54(3)	49(2)	C(29)	9653(5)	10274(4)	2394(5)	75(3)
C(13)	5248(5)	8689(4)	−421(5)	56(3)	B(1)	7814(4)	3530(3)	2636(3)	80(7)
C(14)	4715(5)	8737(4)	−1641(5)	64(3)	F(1)	7502	2814	1835	138(5)
C(15)	5628(5)	8977(4)	−1912(5)	57(3)	F(2)	7740	4366	2084	129(5)
C(16)	4681(4)	8452(4)	347(5)	78(3)	F(3)	8991	3404]	3502	117(3)
C(17)	5589(5)	9124(4)	−3096(4)	81(3)	F(4)	7043	3537	3134	131(4)
C(18)	7889(5)	9257(4)	−694(4)	62(3)	B(10)	7428(9)	3521(8)	2369(9)	97(10)
C(19)	8538(4)	9979(4)	257(4)	63(3)	F(10)	7793	2626	2307	135(10)
N(21)	8345(4)	10367(3)	3375(4)	55(2)	F(20)	6542	3788	1272	112(5)
N(22)	7742(4)	9535(3)	3001(4)	54(2)	F(30)	8400	4116	2731	98(6)
C(23)	7344(5)	9324(4)	3800(5)	56(3)	F(40)	6961	3551	3157	101(7)
C(24)	7688(5)	10010(4)	4646(5)	65(3)					

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Description of the Crystal Structure of $[Co(ddaH)Cl](BF_4)$. The asymmetric unit consists of one molecule of $[Co(ddaH)Cl]^+$ and one non-coordinating tetrafluoroborate anion. The coordination sphere of the copper(II) atom is filled with two pyrazole nitrogens with both copper-nitrogen distances of 1.98 Å and one amine nitrogen with a copper−nitrogen distance of 2.06 Å. The chloride-copper distance is 2.21 Å. Other relevant bond distances and angles are given in Table 3d. The coordination geometry around the copper(II) atom can be described as distorted tetrahedral. No other potential ligands are within semi-coordination distance of Co(II), as deduced from the Co(1)−F(40) distance of 5.94(1) Å. The tetrafluoroborate anion is disordered, however, both orientations used for the description of the disorder show the presence of a weak hydrogen bridge, N(10)−F(3) = 2.93(8) Å and N(10)−F(30) = 2.92(0) Å. Stacking of the pyrazole rings in the structure is not observed.

Comparison of the Crystal Structures. Comparison of the two crystal structures with the formula $[M(ddaH)Cl]_2(MCl_4)$ shows that both compounds are very much alike. The metal-ligand coordination distances are quite the same for both compounds. However, the differences in the coordination angles around the two metal ions are remarkable. The N(10)−M(II)−N(12), Cl−M(II)−N(22) and N(10)−M(II)−N(22) angles in

Table 3. Selected Bond Lengths (Å) Involving Non-Hydrogen Atoms and Selected Bond Angles (deg)

a. $[Cu(ddaH)Cl]_2(CuCl_4)$ (**A**)			
Cu(1)−Cl(1)	2.232(3)	Cu(2)−Cl(2)	2.215(3)
Cu(1)−N(10)	2.022(7)	Cu(2)−Cl(3)	2.282(3)
Cu(1)−N(12)	1.999(8)	Cu(2)−Cl(2A)	2.215(3)
Cu(1)−N(22)	1.980(7)	Cu(2)−Cl(3A)	2.282(3)
Cl(1)−Cu(1)−N(10)	138.6(2)	Cl(2)−Cu(2)−Cl(3A)	100.8(1)
Cl(1)−Cu(1)−N(12)	100.2(2)	Cl(3)−Cu(2)−Cl(3A)	117.8(2)
N(10)−Cu(1)−N(12)	96.1(3)	Cl(2A)−Cu(2)−Cl(3A)	101.0(1)
Cl(1)−Cu(1)−N(22)	97.0(2)	Cu(1)−N(10)−C(19)	116.5(5)
N(10)−Cu(1)−N(22)	93.5(3)	Cu(1)−N(10)−C(29)	118.9(5)
N(12)−Cu(1)−N(22)	141.1(3)	Cu(1)−N(12)−N(11)	123.6(6)
Cl(2)−Cu(2)−Cl(3)	101.0(1)	Cu(1)−N(12)−C(13)	130.8(6)
Cl(2)−Cu(2)−Cl(2A)	137.0(2)	Cu(1)−N(22)−N(21)	124.7(5)
Cl(3)−Cu(2)−Cl(2A)	100.8(1)	Cu(1)−N(22)−C(23)	129.4(6)
b. $[Co(ddaH)Cl]_2(CoCl_4)$ (**B**)			
Co(1)−Cl(1)	2.216(1)	Co(2)−Cl(2)	2.289(1)
Co(1)−N(10)	2.068(3)	Co(2)−Cl(3)	2.255(2)
Co(1)−N(12)	1.982(3)	Co(2)−Cl(2A)	2.289(1)
Co(1)−N(22)	2.004(3)	Co(2)−Cl(3A)	2.255(2)
Cl(1)−Co(1)−N(10)	112.1(1)	Cl(2)−Co(2)−Cl(3A)	107.1(1)
Cl(1)−Co(1)−N(12)	118.1(1)	Cl(3)−Co(2)−Cl(3A)	116.4(1)
N(10)−Co(1)−N(12)	97.5(1)	Cl(2A)−Co(2)−Cl(3A)	110.7(1)
Cl(1)−Co(1)−N(22)	106.7(1)	Co(1)−N(10)−C(19)	114.1(2)
N(10)−Co(1)−N(22)	100.4(1)	Co(1)−N(10)−C(29)	114.1(2)
N(12)−Co(1)−N(22)	120.2(1)	Co(1)−N(12)−N(11)	123.1(2)
Cl(2)−Co(2)−Cl(3)	110.7(1)	Co(1)−N(12)−C(13)	130.8(3)
Cl(2)−Co(2)−Cl(2A)	104.1(1)	Co(1)−N(22)−N(21)	118.0(2)
Cl(3)−Co(2)−Cl(2A)	107.1(1)	Co(1)−N(22)−C(23)	130.5(3)
c. $[Cu(ddaH)Cl](BF_4)$ (**C**)			
Cu(1)−Cl(1)	2.247(3)	B(1)−F(1)	1.338(24)
Cu(1)−N(10)	2.038(9)	B(1)−F(2)	1.334(24)
Cu(1)−N(12)	1.977(8)	B(1)−F(3)	1.377(27)
Cu(1)−N(22)	1.962(9)	B(1)−F(4)	1.276(23)
Cl(1)−Cu(1)−N(10)	130.9(3)	Cu(1)−N(22)−N(21)	124.3(7)
Cl(1)−Cu(1)−N(12)	95.4(3)	Cu(1)−N(22)−C(23)	131.4(7)
N(10)−Cu(1)−N(12)	94.8(3)	F(1)−B(1)−F(2)	108.5(17)
Cl(1)−Cu(1)−N(22)	95.9(3)	F(1)−B(1)−F(3)	107.9(16)
N(10)−Cu(1)−N(22)	94.5(4)	F(2)−B(1)−F(3)	109.0(17)
N(12)−Cu(1)−N(22)	155.0(4)	F(1)−B(1)−F(4)	108.8(18)
Cu(1)−N(10)−C(19)	115.4(6)	F(2)−B(1)−F(4)	114.5(17)
Cu(1)−N(10)−C(29)	116.5(7)	F(3)−B(1)−F(4)	107.9(17)
d. $[Co(ddaH)Cl](BF_4)$ (**D**)			
Co(1)−Cl(1)	2.207(2)	B(1)−F(3)	1.372(9)
Co(1)−N(10)	2.057(5)	B(1)−F(4)	1.368(9)
Co(1)−N(12)	1.977(3)	B(10)−F(10)	1.370(9)
Co(1)−N(22)	1.985(5)	B(10)−F(20)	1.373(2)
B(10)−F(1)	1.368(5)	B(10)−F(30)	1.367(9)
B(1)−F(2)	1.369(6)	B(10)−F(40)	1.371(6)
Cl(1)−Co(1)−N(10)	110.7(1)	F(1)−B(1)−F(2)	109.9(1)
Cl(1)−Co(1)−N(12)	112.0(1)	F(1)−B(1)−F(3)	109.2(9)
N(10)−Co(1)−N(12)	97.6(2)	F(2)−B(1)−F(3)	108.7(3)
Cl(1)−Co(1)−N(22)	113.6(1)	F(1)−B(1)−F(4)	109.6(2)
N(10)−Co(1)−N(22)	98.1(2)	F(2)−B(1)−F(4)	109.7(1)
N(12)−Co(1)−N(22)	121.8(2)	F(3)−B(1)−F(4)	109.5(3)
Co(1)−N(10)−C(19)	112.6(3)	F(10)−B(10)−F(20)	109.2(3)
Co(1)−N(10)−C(29)	113.5(4)	F(10)−B(10)−F(30)	109.7(7)
Co(1)−N(12)−N(11)	122.2(3)	F(20)−B(10)−F(30)	109.4(9)
Co(1)−N(12)−C(13)	132.3(4)	F(10)−B(10)−F(40)	109.4(7)
Co(1)−N(22)−N(21)	122.8(4)	F(20)−B(10)−F(40)	109.2(5)
Co(1)−N(22)−C(23)	131.5(4)	F(30)−B(10)−F(20)	109.6(3)

both compounds are comparable. But the Cl−Cu−N(10) and Cl−Co−N(10) (138.6(2) and 112.1(1)°, respectively), the Cl−Cu−N(12) and Cl−Co−N(12) (100.2(2) and 118.1(1)°, respectively) and the N(12)−Cu−N(22) and N(12)−Co−N(22) (141.1(3) and 120.2(1)°, respectively) are significant different. From these bond angles it can be concluded that the deviation from an ideal tetrahedral arrangement is much more prominent in the copper(II) compound. Thus, both compounds have a distorted tetrahedral coordination environment, but the $[Cu(ddaH)Cl]^+$ cation is significantly more distorted which most probably originates from a Jahn−Teller effect. Looking at the bond angles of the $(MCl_4)^{2-}$ anions it can be concluded that both anions also are distorted tetrahedrons. The $(CuCl_4)^{2-}$ anion shows a significantly larger aberration from an ideal tetrahedron than the $(CoCl_4)^{2-}$ anion. The $(CuCl_4)^{2-}$ anion has four Cl−Cu(II)−Cl angles in the range 100−103° and the other two enlarged to 117.8 and 137.0°. According to Greenwood[16] these angles are typical for a Jahn−Teller distorted tetrahedral $(CuCl_4)^{2-}$ anion. Both tetrachlorometalate(II) anions are moderately strong hydrogen bridged to the amine nitrogen of the ligand.

Considering the two crystal structures with the general formula $[M(ddaH)Cl](BF_4)$, it can be seen that the cationic part of both compounds is almost identical with the cationic part of the $[M(ddaH)Cl]_2(MCl_4)$ compounds. The metal−ligand coordination distances of all four compounds are very much alike. Especially the bond angles in the cation of the two cobalt(II) containing structures are in good agreement with each other. In the $[Cu(ddaH)(Cl](BF_4)$ is also a Jahn−Teller effect present. In the $[M(ddaH)Cl](BF_4)$ compounds are besides normal van der Waals forces, also weak hydrogen bridges present from the tetrafluoroborate anion to the amine nitrogen of the ddaH ligand.

The copper(I) tetrafluoroborate compound synthesized by Sorrell and co-workers[7] is a three-coordinate complex having a T-shaped geometry around the Cu(I) metal ion. Unfortunately no X-ray structure determination was performed on this compound, therefore comparison of bond angles and distances with the structures presented in this paper is not possible. The copper(II) nitrate and copper(II) perchlorate complexes synthesized by Martens[11] are respectively six- and five-coordinate complexes. The structures of both compounds were determined by X-ray diffraction. The $[Cu(ddaH)(NO_3)_2]$ compound has a distorted octahedral coordination geometry around the copper atom and the $[Cu(ddaH)(ClO_4)(CH_3CH_2OH)](ClO_4)$ compound has a distorted trigonal bipyrimidal coordination environment. The copper(II) pyrazole nitrogen bond distances in these compounds vary between the 1.92(2) and 1.97(7) Å, and the copper(II) amine−nitrogen distances are between 2.00(1) and 2.03(2) Å. The Cu−N distances of the coordination compounds described in this paper are very much in agreement with the above mentioned values. The bond angles in the compounds described in this paper are not comparable with the bond angles described by Martens,[11] because of the totally different coordination geometries around the metal ion.

Spectroscopic Results. In Table 4 the colors, melting points, metal contents, ligand field data, and EPR data for the five complexes with ddaH are given. In all cases cations with only one ligand coordinated to the central metal ion were found. Attempts to obtain cationic complexes with a metal to ligand ratio of 1:2 were not successful. Those 1:2 complexes could also not be obtained with the related ligand bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ethylamine (abbreviated ddae).[17] As in the case of ddae it can be concluded that steric factors prevent the formation of 1:2 complexes with ddaH. The four-bond chelate bites[18] of ddaH cause the N−M(II)−N coordination angles to be larger than 90°, thereby pushing the methyl substituents on

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Table 4. Relevant Characterization and Analytical Data (Calculated Values in Parentheses) for the Coordination Compounds with ddaH (Denoted by L)

compound	color	mp (°C)	% M	electronic bands (10^3 cm^{-1})	EPR *g* values
$[Cu(L)Cl]_2(CuCl_4)$	green	182	20.0 (20.6)	9.7, 14.1	2.24, 2.10
$[Co(L)Cl]_2(CoCl_4)$	blue	225	19.1 (19.4)	5.6,^{a} 6.3, 9.3, 10.7, 14.0,^{a} 14.8,^{a} 16.1, 17.1 (sh), 19.2	
$[Cu(L)(Cl)(BF_4)$	green	184	13.6 (13.7)	14.3	2.14
$[Co(L)(Cl)(BF_4)$	blue	202	12.9 (12.8)	(6.5),^{b} 9.8, 114, (ν_2),^{c} 17.0, 19.5 (ν_3)	
$[Zn(L)Cl]_2(ZnCl_4)$	white	215	20.7 (21.1)		

^{a} $(CoCl_4)^{2-}$ absorptions. ^{b} Very weak and broad. ^{c} $\nu_2 = {}^4T_1(F) \leftarrow {}^4A_2$. ^{d} $\nu_3 = {}^4T_1(P) \leftarrow {}^4A_2$.

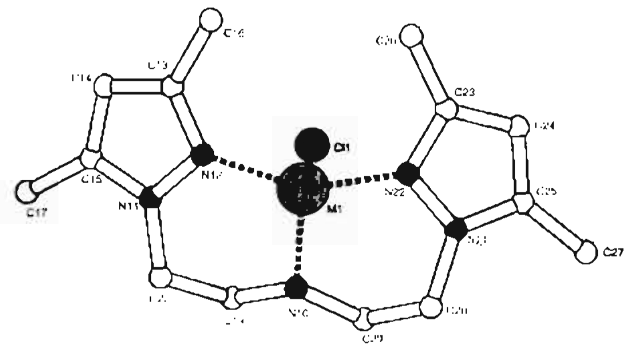

Figure 2. PLUTON[15] projection and atomic labeling of the cation $[M(ddaH)Cl]^+$. For clarity the hydrogen atoms are omitted.

the pyrazole ring inward. In this way the approach of another ddaH ligand to the M^{2+} metal ion is sterically prevented.

In the infrared spectra of the $[M(ddaH)Cl]_2(MCl_4)$ compounds the N−H stretching vibrations of Cu(II), Co(II), and Zn(II) are respectively 3080, 3230, and 3160 cm^{-1}. For the $[M(ddaH)Cl](BF_4)$ compounds with Cu(II) and Co(II) these vibrations are respectively 3240 and 3260 cm^{-1}. Infrared spectra taken of the coordination compounds in either a KBr medium or in a $CHCl_3$ medium were virtually identical. The free N−H stretching vibration of the ddaH ligand was taken at 3440 cm^{-1}, according to literature values for secundary amines.[19] Observation of this band for the free ligand is not possible because of intramolecular H-bonding. The N−Cl distances and the N−F distances in the hydrogen bridges have been correlated with the position of the N−H stretching vibrations in the infrared spectra, according to the relationship of Bellamy and Owen.[20] It appeared that the observed N−Cl and N−F bond distances in the Co(II) coordination compounds are in very good agreement and within experimental error of the calculated bond distances. However, the observed N−Cl or N−F bond distances in the Cu(II) compounds deviate slightly from the calculated distances, *i.e* 3.20 Å (calculated) compared to 3.26 Å for the $[Cu(ddaH)Cl]_2(CuCl_4)$ compound and 2.90 Å (calculated) compared to 3.04 Å for the $[Cu(ddaH)Cl](BF_4)$ compound. The extra shift in the ν_s(N−H) absorptions for the Cu(II) compounds are ascribed to a stronger M(II)−N bonding for Cu(II) compared to Co(II), as also is seen from the shorter M(II)−N bonds in the Cu(II) coordination compounds.

Absorptions due to hydrogen-bridged BF_4^- ion vibrations have been observed at 330/380 (ν_2), 525/523 (ν_4), 770/768 (ν_1) and 1070/1050 (ν_2) cm^{-1} [21,22] for the Co(II)/Cu(II) compound. Vibrations located at 310 and 345 cm^{-1} in the infrared spectra of the $[M(ddaH)Cl](BF_4)$ compounds were not observed in the spectrum of ddaH and are most probably due to respectively Cu−Cl and Co−Cl vibrations[19] of the cation. The Co−Cl stretching vibrations in the $(CoCl_4)^{2-}$ anion[22−24] are positioned at 278 (ν_1) and for ν_3 at 295 and 305 cm^{-1}. The vibrational modes for the $(CuCl_4)^{2-}$ ion occur in the far-IR[19,23−25] and normally only the ν_3 vibration is seen. Unfortunately no vibrational modes in the IR-spectrum could be ascribed to the $(CuCl_4)^{2-}$ ion. Cu−Cl and Co−Cl vibrations in the cation of the $[M(ddaH)Cl]_2(MCl_4)$ compounds are observed at 330 and 335 cm^{-1}, respectively. All compounds show a small shift (5−7 cm^{-1}) of the pyrazole ring deformation vibration (1555 cm^{-1}) upon coordination of the metal ion to lower frequencies. The $[Zn(ddaH)Cl]_2(ZnCl_4)$ is IR isomorphous with the corresponding Cu(II) and Co(II) compounds. A possible Zn−Cl vibration was observed at 330 cm^{-1}.

The $[Cu(ddaH)Cl]_2(CuCl_4)$ compound shows two absorption maxima in the ligand field spectrum (Table 4) due to the two different Cu(II) species that are present. Comparing these maxima with the absorption shown by the $[Cu(ddaH)Cl](BF_4)$ compound, it can be concluded that the absorption at 9.7 × 10^3 cm^{-1} should be ascribed to the $(CuCl_4)^{2-}$ ion. This is also in agreement with the literature.[25] The vis−near-IR spectrum of $[Co(ddaH)Cl]_2(CoCl_4)$ shows five absorption maxima, which according to the literature[26] can be ascribed to pseudotetrahedral absorptions with symmetries lower than tetrahedral. The ligand field spectrum of $[Co(ddaH)Cl]_2(CoCl_4)$ in fact comprises two spectra; one of the $(CoCl_4)^{2-}$ ion and one of the cation. The d−d transitions at 5.6 × 10^3 cm^{-1}, 14.0 × 10^3 cm^{-1}, and 14.8 × 10^3 cm^{-1} can be assigned to the tetrachlorocobaltate(II);[16,25,27] the other transitions (Table 4) belong to the cation. The ligand field data of the two Co(II) cations are very much in agreement, except for the additional absorption at 16.1 × 10^3 cm^{-1} for the $[Co(ddaH)Cl]_2(CoCl_4)$ compound. According to Wellon et al.[27] the splitting of the ν_3 in three bands is not unusual for lower symmetrics.

The EPR spectrum of $[Cu(ddaH)Cl](BF_4)$ shows an isotropic signal with $g_{iso} = 2.12$. This is most likely due to exchange narrowing as a result of the lattice packing effects. EPR spectra taken in nitromethane/MeOH (2/10) or MeOH/toluene (1/10) at 77 K did not result in a better resolution of the *g*-anisotropy and hyperfine structure. The EPR spectrum of $[Cu(ddaH)Cl]_2(CuCl_4)$ shows an axial signal with a $g_\parallel$ value of 2.24 and a $g_\perp$ value of 2.10. No separate signal due to the $(CuCl_4)^{2-}$ anion was observed. This signal is probably obscured by the $[Cu(ddaH)Cl]^+$ signal. EPR spectra taken in MeOH/toluene (1/10) at 77 K did not result in a better resolution. According to the literature,[28] the $(CuCl_4)^{2-}$ anion has a $g_\parallel$ value of 2.40 and a $g_\perp$ value of 2.76.

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Concluding Remarks

The results of the present investigations show that only 1:1 (metal:ligand) cationic complexes are obtained with the tridentate ligand ddaH. When chloride is used as anion autodissociation with formation of $(MCl_4)^{2-}$ takes place with the metals Cu(II), Co(II) and Zn(II). This behavior suggests that the ligand ddaH favors the formation of the $[M(ddaH)Cl]^+$ cation with a distorted tetrahedral geometry. In the presence of the large BF_4^- anion autodissociation does not occur, while the distorted tetrahedral $[M(ddaH)Cl]^+$ cation can still be formed. When other anions than chloride are used like perchlorate or nitrate, distorted five- or six-coordinate structures[11] are formed.

The formation of a tetrametalate(II) anion in the ion-exchange experiments[10] can most probably be ruled out. Comparison of the ligand field data of the homogeneous phase Cu(II) complexes and the heterogeneous phase Cu(II) complexes indicates that the absorption due to the $CuCl_4^{2-}$ anion is not present in the heterogeneous phase. When other anions besides chloride are present in the homogeneous phase autodissociation, and thus formation of $CuCl_4^{2-}$, does not occur. In the ion-exchange experiments acetate ions besides chloride ions are present, which will prevent the autodissociation reaction. Experiments designed to obtain coordination compounds with acetate as the anion failed to yield crystalline products. Whether the Cu^{2+} ions on the polymer are present in a distorted tetrahedral coordination geometry is uncertain, but cannot be ruled out. Because Co(II) is hardly taken up by the resin in the ion-exchange experiments no reasonable ligand field spectra could be taken.[10] Therefore comparison with the ligand field spectra of the Co(II) coordination compounds is unfortunately impossible.

The position of the N−H stretching vibration in the infrared spectra is determined by the strength of the M(II)−N−H bond and by the strength of the hydrogen bond (N−H- - -Cl or N−H- - -F). According to the literature,[19] the N−H stretching vibration shifts to lower wavenumbers if these bonds become stronger. It was observed that only the N−H bond distances for the Co(II) compounds are in complete agreement with the Bellamy and Owen relationship. For the Cu(II) compounds, the calculated N−H bond distances deviate somewhat from the Bellamy and Owen relationship. The ν_s(N−H) are shifted to lower wave numbers than calculated, which has been interpreted as resulting from stronger M(II)−N bonds in the Cu(II) coordination compounds.

In the ion-exchange experiments, when the ligand is anchored onto a solid support, a very selective uptake behaviour towards Cu(II) has been observed.[10] Although all metal ions presented in this paper have almost identical coordination geometries in the homogeneous phase, discrimination between the different metal ions in the heterogeneous phase takes place. This is most probably due to the fact that the complexes formed with Cu(II) are generally more stable. Distribution coefficient experiments with the corresponding ion exchanger show that Cu^{2+} forms the most thermodynamically stable complexes in the presence of chloride and acetate ions.[10]

When other anions, *i.e* BF_4^- and NO_3^-, are used in the metal-uptake experiments slightly different uptake patterns were observed, although the metal uptake was still selective towards Cu^{2+} ions.[10] This is most probably due to changes in coordination geometry around the metal ion. This is underlined by the homogeneous phase complexes of Martens, *i.e* different coordination geometries around the Cu^{2+} ion were found by changing the anion.[11] So besides stability of the formed complexes also the coordination geometry is of importance in ion-exchange procedures.

Supplementary Material Available: Listings of the atomic coordinates and the isotropic displacement coefficients of the hydrogen atoms, the non-hydrogen anisotropic temperature factors, and elemental analyses (9 pages). Ordering information is given on any current masthead page.