DOI: 10.1002/ejic.201001231

From a Simple Pyrazole-Derived 1,2-Amino Alcohol to Mono- and Multinuclear Complexes by Tailoring Hydrogen Bond Patterns

Christoph K. Seubert,[a] Yu Sun,[a] Yanhua Lan,[b] Annie K. Powell,[b] and Werner R. Thiel*[a]

Keywords: Coordination chemistry / Hydrogen bonds / N ligands / Multinuclear complexes / Magnetic properties / Amino alcohols

Starting from easily accessible ethyl-5(3)-methylpyrazole-3(5)-carboxylate, 2-[(1,5-dimethyl)pyrazol-3-yl]propan-2-ol (**3**) can be obtained in good yields in just two steps. The latter compound undergoes coordination to a series of transition metal ions; the resulting complexes were characterized by means of spectroscopy and magnetic measurements.

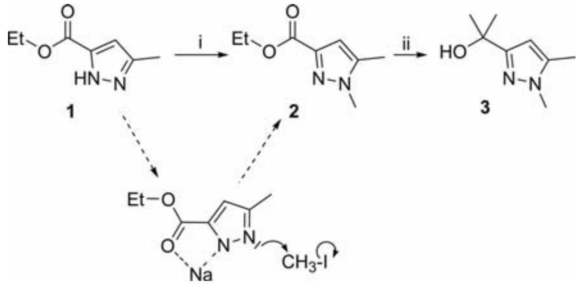
Introduction

Amino alcohols have found wide applications as ligands in coordination chemistry for quite some time. They have been used in enantioselective catalysis[1] as well as for Metal-Organic Chemical Vapour Deposition[2] and other purposes. In the past, we established an efficient method to generate enantiomerically pure chiral 1,3-amino alcohols bearing a pyrazole donor by the ring opening of epoxides, followed by an enzymatic kinetic resolution. However, 1,2-amino alcohols with a pyrazole fragment as the *N*-donor site have rarely been reported in the literature, although the pyrazole moiety allows the simple introduction of electron donating or withdrawing substituents and thus enables a fine-tuning of the electronic properties of the ligand.[3] They can be accessed by [2+3] cycloaddition reactions of diazomethane to functionalised prop-1-en-2-ols[4] and used for pharmaceutical applications.[5] Only a few metal complexes carrying a hydroxymethylpyrazole as the chelating ligand have been reported until now, most are coordinated with a hydroxymethyl-functionalised pyrazolylborate ligand.[6] Herein we present a rapid and non-toxic route to a novel 3-hydroxymethyl functionalised pyrazole and a series of transition metal complexes derived from this ligand.

Results and Discussion

Ligand Synthesis and Characterization

As outlined in Scheme 1, the synthesis of ligand **3** follows a two-step procedure starting from easily available ethyl-5(3)-methylpyrazole-3(5)-carboxylate (**1**).[7] The intermediate **2** had already been described in the literature, but the published routes either gave a mixture of two regioisomers[8] or used complex starting materials.[9]



Scheme 1. I) NaH, CH_3I, THF, room temp., 16 h; ii) MeMgCl, THF, reflux., 16 h (this step was carried out twice).

Based on experiments on the regioselective *N*-alkylation of pyrazolylpyridines[10] and 3-(2-hydroxyphenyl)pyrazole[11] it seemed likely that by deprotonation of the pyrazole NH unit of **1** with NaH and subsequent alkylation of the resulting anion with CH_3I, the desired regioisomer **2** should be accessible with high selectivity. Whenever there is a chance for a pyrazolide anion to undergo chelation to a metal cation (here Na^+), alkylation occurs at the “free” nitrogen atom. As expected only traces of the undesired regioisomer were formed, proving that even in the presence of a rather poor donor, such as an ester group, this strategy works.

The proton at the 4-position at the pyrazole ring of **2** shows the typical shift to higher field (δ = 6.34 ppm) in the ^1H NMR spectrum compared with that of **1**, the two methyl groups attached to the pyrazole ring can clearly be distinguished by their specific chemical shifts in the ^1H NMR spectrum [δ = 3.65 (NCH_3) and 2.10 ppm (5-CH_3)] and in the ^{13}C NMR spectrum [δ = 36.5 (NCH_3) and 10.7 ppm (5-CH_3)].

---

[a] Fachbereich Chemie, TU Kaiserslautern,
Erwin-Schrödinger-Str. Geb. 54, 67663 Kaiserslautern, Germany
Fax: +49-631-2054647
E-mail: thiel@chemie.uni-kl.de
[b] Karlsruher Institut für Technologie (KIT), Institut für Anorganische Chemie,
Engesserstr. 15, 76131 Karlsruhe, Germany

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201001231.

The desired 2-[(1,5-dimethyl)pyrazol-3-yl]propan-2-ol (**3**) was prepared by treating **2** with an excess of MeMgCl in THF, a procedure that was required to be repeated since after the first conversion compound **3** was obtained in a mixture with a large amount of methyl (1,5-dimethylpyrazol-3-yl) ketone. The ^{1}H NMR spectrum ($CDCl_3$) of **3** exhibits four singlets in a 6:3:3:1 ratio at δ = 1.43, 2.12, 3.60 and 5.83 ppm corresponding to the $C(OH)(CH_3)_2$, $C_{pz}CH_3$, NCH_3 and C_{pz}–H protons, respectively. Highly pure **3** can be obtained by sublimation, leading directly to single crystals suitable for X-ray diffraction analysis (Figure 1).

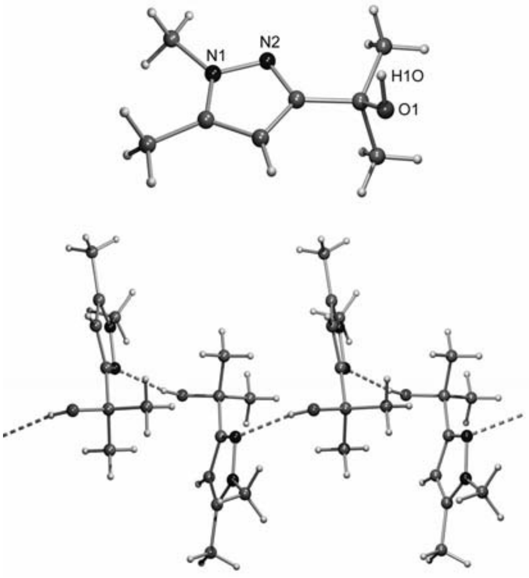


Figure 1. Molecular structure of **3** in the solid state (top), formation of chains by hydrogen bonds (bottom). Characteristic lengths [Å] and angles [°] of the hydrogen bond: O1–H1O 0.84, H1O···N2 2.10, O1···N2 2.930(2), O1–1O···N2 169.00.

The X-ray structure analysis proved that the desired regioisomer was formed. As shown in Figure 1, compound **3** forms chains by intermolecular hydrogen bonds between the OH group and the N2 atom of the pyrazole ring. The OH proton is not located in the plane of the pyrazole ring, it forms an angulated hydrogen bond of moderate strength[12] corroborating the low melting and sublimation temperatures of compound **3**. Typically for alcohols undergoing hydrogen bonding, a strong absorption at 3353 cm^{-1} is observed in the IR spectrum of compound **3**; the C=O absorption of the starting material is no longer present.

Synthesis, Characterization and Molecular Structures of the Metal Complexes

To investigate the coordination chemistry of compound **3**, the ligand was treated with a series of different transition metal dichlorides in a 2:1 ratio in appropriate solvents. Since the ligand is able to coordinate in a mono- and a bidentate fashion and also provides an OH proton for hydrogen bond formation, a variety of different coordination geometries depending on the metal site could be expected.

The treatment of two equivalents of **3** with the labile benzonitrile complex $Pd(PhCN)_2Cl_2$ in CH_2Cl_2 solution gave the desired palladium(II) complex **4** as a yellow solid. It was characterized by IR and NMR spectroscopies and elemental analysis. In the IR spectrum, the OH stretching frequency was observed at 3468 cm^{-1}, indicating a stronger OH bond due to a weaker hydrogen bond compared with the free ligand **3**. Whereas the ^{1}H NMR resonance of the proton in the 4-position of the pyrazole ring stays almost unaffected (δ = 5.94 ppm), all other resonances are shifted to lower field compared with **3**, the signal of the NCH_3 group (δ = 4.66 ppm) is shifted by more than 1 ppm. Crystallization from $CHCl_3/Et_2O$ resulted in the formation of yellow prisms suitable for X-ray structure analysis (Figure 2).

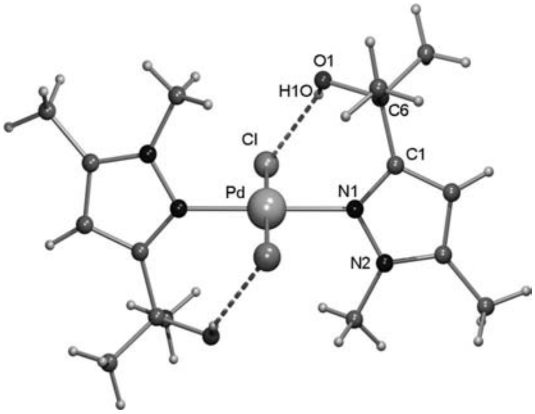


Figure 2. Molecular structure of **4** in the solid state; characteristic bond lengths [Å], angles [°] and dihedral angles [°]: Pd1–Cl1 2.3102(4), Pd1–N1 2.0138(13), O1–H1O 0.84, H1O···Cl1 2.45, O1···Cl1 3.1844(12), Cl1–Pd1–N1 91.23(3), Cl1–Pd1–N1a 88.77(3), O1–H1O···Cl1 146.00, Cl1–Pd1–N1–N2 –104.47(9), Cl1–Pd1–N1–C1 83.61(12), Pd1–N1–C1–C6 –4.6(2), N1–C1–C6–O1–21.71(18).

As expected, the palladium(II) centre is coordinated in a square-planar geometry with the two pyrazole ligands in a *trans* orientation. There is no coordination of the hydroxy groups, they undergo intramolecular hydrogen bond formation with the chloro ligands. This mode of coordination is consistent with reports in the literature; compounds of the type $(pyrazole)_2PdCl_2$ are generally found in *trans* geometry[13] except in systems in which pyrazole rings are part of a macrocycle.[14] All bond parameters of **4** are in agreement with data from the literature.[13] The metal site of **4** is located in a centre of inversion, leading to a coplanar orientation of the two pyrazole rings. The rather long distance H1O···Cl1 (2.45 Å) is consistent with a moderate to weak hydrogen bond.[12]

The reaction of two equivalents of **3** with $CuCl_2$ in acetone solution afforded a green solid. After recrystallization from $CHCl_3/Et_2O$ the copper(II) complex **5** could be isolated in 76% yield as green prisms suitable for X-ray structure analysis (Figure 3). Again, two ligands are coordinated to the metal centre. Here, however, the ligands are found in a bidentate *N*,*O*-coordination mode resulting in a five coordinate cationic metal centre with the additional chloride ion as the counter anion. This is in contrast to the dichloro copper complex of the ligand *trans*-2-pyrazol-1-ylcyclohexan-1-ol,[15] in which a distorted octahedral coordination environment is observed. This may be due to an enhanced steric hindrance caused by the substitution pattern at the pyrazole ring of **3** and by the smaller ring size of the resulting metallacycle. The coordination geometry of the copper(II) ion in **5** is neither square pyramidal nor trigonal bipyramidal ($\tau = 0.501$) but almost exactly in the middle between these two geometries. Until now cationic copper(II) complexes of the type $[CuO_2N_2Cl]^+$ have only been described with pyridine as the *N*-donor ligand.[16] In compound **5**, the two nitrogen atoms as well as the two oxygen donor atoms are located in positions *trans* to each other. The Cu–N1/Cu–N3/Cu–O/Cu–Cl distances are typical for copper pyrazole/alcohol/chloro complexes.[15–17] By hydrogen bond formation between the OH groups and the chloride anions, a polymeric chain structure is established as shown in Figure 3.

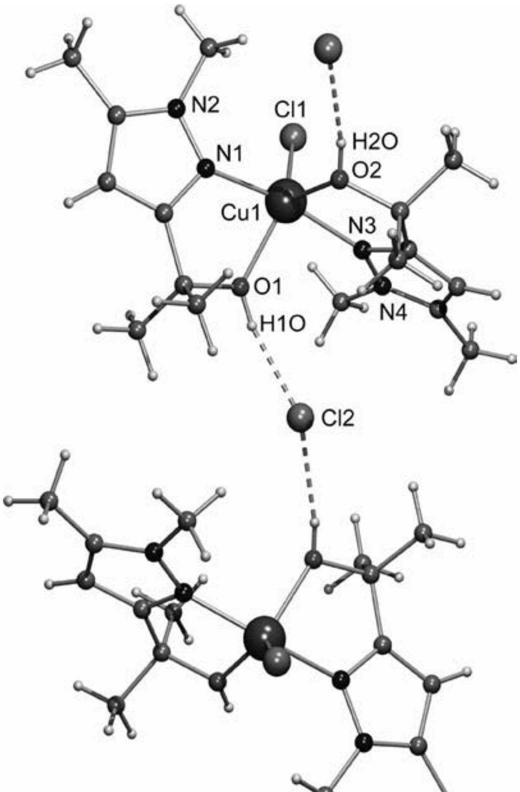


Figure 3. Molecular structure of **5** in the solid state including chain formation by hydrogen bonds. Characteristic bond lengths [Å], angles [°] and dihedral angles [°]: Cu1–Cl1 2.2426(7), Cu1–O1 2.044(2), Cu1–O2 2.138(2), Cu1–N1 1.977(2), Cu1–N3 1.961(2), O1–H1O 0.83(3), H1O···Cl2 2.14(3), O1···Cl2 2.950(2), O2–H2O 0.804(19), H2O···Cl2 2.20(2), O2···Cl2 2.989(2), Cl1–Cu1–O1 134.20(7), Cl1–Cu1–O2 120.48(7), Cl1–Cu1–N1, 98.86(7), Cl1–Cu1–N3 96.86(6), O1–Cu1–O2 105.23(9), O1–Cu1–N1 77.83(9), O1–Cu1–N3 90.45(9), O2–Cu1–N1 96.18(9), O2–Cu1–N3 76.58(9), N1–Cu1–N3 164.25(9), Cu1–O1–C6 118.83(15), Cu1–O2–C14 117.75(16), Cu1–O1–H1O 131(2), Cu1–O2–H2O 124(2), O1–H1O···Cl2 168(3), O2–H2O···Cl2 168(3).

The reaction of two equivalents of **3** with $CoCl_2{\cdot}(H_2O)_6$ or $NiCl_2{\cdot}(H_2O)_6$ in methanol afforded blue **6** and green **7** in 87 and 83% yield, respectively, after recrystallization from $MeOH/Et_2O$. Both compounds are isostructural and crystallize in the monoclinic space group $P2_1/n$ with nearly identical cell parameters and interatomic distances and angles. A similar behaviour was previously observed for the dichlorocobalt(II) and dichloronickel(II) complexes of 3(5)-(4-methoxyphenyl)pyrazole.[18] In the following section, the solid-state structure of the cobalt(II) complex **6** (Figure 4) shall be discussed; the structural data of the nickel(II) complex **7** can be found in the Supporting Information.

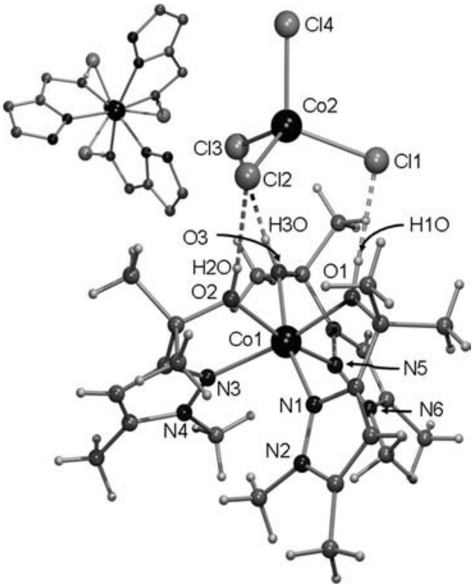


Figure 4. Solid state structure of **6**, the inset shows the view along the Co1···Co2 axis. Characteristic bond lengths [Å], angles [°]: Co1–O1 2.105(3), Co1–O2 2.080(3), Co1–O3 2.100(3), Co1–N1 2.109(3), Co1–N3 2.109(3), Co1–N5 2.088(3), Co2–Cl1 2.2811(13), Co2–Cl2 2.2982(12), Co2–Cl3 2.2875(10), Co2–Cl4 2.2525(11), O1–H1O 0.843(19), H1O···Cl1 2.26(2), O1···Cl1 3.096(3), O2–H2O 0.84(3), H2O···Cl2 2.25(3), O2···Cl2 3.090(3), O3–H3O 0.83(3), H3O···Cl3 2.28(3), O3···Cl3 3.105(3), O1–Co1–O2 90.68(11), O1–Co1–O3 86.89(10), O1–Co1–N1 74.68(10), O1–Co1–N3 166.09(12), O1–Co1–N5 93.27(11), O2–Co1–O3 90.73(10), O2–Co1–N1 95.46(11), O2–Co1–N3 75.43(11), O2–Co1–N5 165.50(10), O3–Co1–N1 160.58(12), O3–Co1–N3 93.69(12), O3–Co1–N5 75.59(10), N1–Co1–N3 105.68(13), N1–Co1–N5 99.04(12), N3–Co1–N5 100.34(11), Cl3–Co2–Cl4 110.04(5), Cl1–Co2–Cl4 111.70(4), Cl1–Co2–Cl2 110.39(5), Cl1–Co2–Cl3 107.33(4), Cl2–Co2–Cl3 109.17(5), Cl2–Co2–Cl4 108.19(4), O1–H1O···Cl1 172(3), O2–H2O···Cl2 175(3), O3–H3O···Cl3 177(3).

The crystal structure revealed that the expected complex with two bidentate coordinated ligand molecules and two chloride ligands was not formed. Here one octahedrally coordinated $[CoL_3]^{2+}$ cation is accompanied by a $[CoCl_4]^{2-}$ anion. The nitrogen atoms of the three chelate ligands are found coordinating facially and the three oxygen atoms are located on the opposite triangle of the octahedron. Thus, the OH groups form a tridentate binding pattern for proton acceptors allowing hydrogen bonds to three chloride ligands of the tetrachlorocobaltate(II) anion. The distances H1O···Cl1 (2.26 Å), H2O···Cl2 (2.25 Å) and H3O···Cl3

(2.28 Å) and the corresponding angles O1–H1O···Cl1 (172°), O2–H2O···Cl2 (175.2°) and O3–H3O···Cl3 (177°) are consistent with weak to moderate hydrogen bonds.[12] The blue colour of crystalline **6** is typical for tetrahedrally coordinated cobalt(II) sites, such as Co2. The blue crystals, however, formed directly from a pink coloured solution. This colour is typical for octahedrally coordinated cobalt(II) in a weak ligand field. From this observation one can conclude, that the tetrachlorocobaltate(II) ion is formed during the crystallization process by a templating effect of the cation.

As expected, the Co2–Cl distances of the chloride ligands involved in hydrogen bonds are slightly longer (0.03–0.05 Å) than Co–Cl4, leading to a slightly distorted tetrahedral coordination geometry of the $[CoCl_4]^{2-}$ anion. The coordination geometry of the Co1 site can be best explained as a distorted, facially coordinated A_3B_3Co octahedron flattened along the vector connecting the centroids of the nitrogen and the oxygen triangle. Whereas there is a whole series of solid-state structures containing the tetrachlorocobaltate(II) anion, in only a few is a threefold hydrogen-bonding situation found.[19] For the tetrachloronickelate(II) anion in complex **7**, no similar hydrogen-bonding pattern has been described until now.[20] There are some examples for *fac*-N_3O_3M systems (M = Co, Ni) containing macrocyclic nitrogen donor sites with three OH groups in side chains,[21] and some *fac*-N_3O_3Ni systems containing aromatic *N*-donor sites in combination with alcohols.[22] Additionally, there is one nickel complex with hydroxiquinoline as the *N*,*O*-donor showing a hydrogen bond motif similar to **7**.[22b] Therein, a *fac*-tris(8-quinolinol)nickel(II) cation forms three hydrogen bonds to a neighbouring *fac*-tris(8-quinolinolato)-nickel(II) anion leading to a dimeric pelton wheel-like structure. The Ni–O and Ni–N distances are in complete agreement with the data of **6** and **7**. In contrast, 2-hydroxymethylpyridine coordinates in a meridional geometry to nickel(II).[22d] It therefore seems likely that under certain conditions, a templating effect leads to the *fac*-A_3B_3M geometry found in the solid-state structures of **6** and **7**. We will now investigate the exchange of the MCl_4^{2-} anions against other systems (e.g., SO_4^{2-}, PO_4^{3-}, etc.) that are able to undergo hydrogen bonding with three proton-donating sites.

From the structural point of view, no magnetic interaction between the two paramagnetic centres should be present as no obvious bridges suitable for superexchange are present; the cation and the anion are linked together through hydrogen bonds. To get an insight into the influence of the hydrogen bonding on the magnetic properties of **6** and **7**, magnetic measurements were carried out (Figure 5). The dc magnetic susceptibility data of the binuclear Ni^{II} complex **7** shows that this compound is likely to be paramagnetic over the whole temperature range. A slightly temperature-dependent slope of the χT product is a consequence of the significant contribution of the single-ion anisotropy of Ni^{II} ions. For the binuclear cobalt(II) complex **6**, the room temperature χT of 5.73 $cm^3\,K\,mol^{-1}$ is much higher than the expected value of 3.75 $cm^3\,K\,mol^{-1}$ for two spin-only cobalt(II) ions ($S = 3/2$) as a result of the strong orbital contribution. The behaviour of the χT curve is typical of the spin-orbital coupling effect in which the χT product continuously decreases on lowering the temperature. Furthermore, a small upturn observed in the χT value below 2.7 K could be due to either the presence of a weak ferromagnetic interaction between the cobalt(II) centres through the hydrogen bonding or the slight canting between the two asymmetric cobalt(II) centres. The phenomenon of spin canting, however, is not evidenced by either the M vs. H or the AC measurements, in which the critical temperature might be too low to be observable in these measurements.

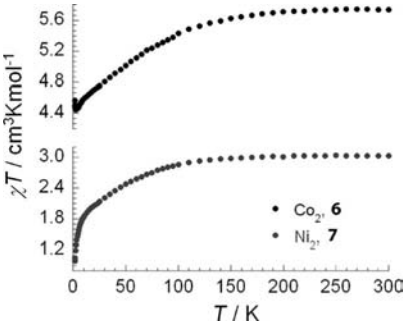


Figure 5. The plots of χT against T under a field of 1000 Oe for compounds **6** and **7**.

The reaction of two equivalents of **3** with $ZnCl_2$ in acetone afforded a colourless solid. After recrystallization from a mixture of $CHCl_3/CH_2Cl_2/Et_2O$, the zinc(II) complex **8** could be isolated in 92% yield as colourless prisms suitable for X-ray diffraction. In this case, only one equivalent of the *N*,*O*-chelate ligand coordinates to the metal centre, the solid-state structure of **8** is shown in Figure 6.

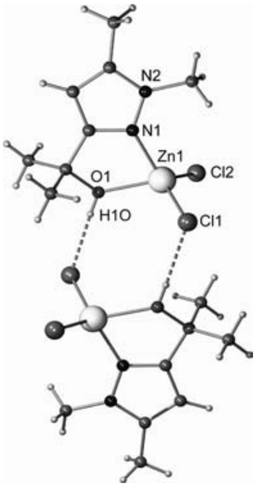


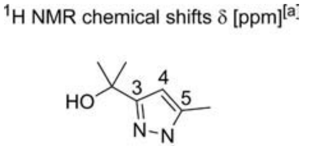
Figure 6. Solid state structure of **8**. Characteristic bond lengths [Å], angles [°] and dihedral angles [°]: Zn1–Cl1 2.2219(7), Zn1–Cl2 2.1905(6), Zn1–O1 2.0579(16), Zn1–N1 1.9986(17), O1–H1O 0.78(2), H1O···Cl1 2.29(2), O1···Cl1 3.0590(17), Cl1–Zn1–Cl2 120.09(3), Cl1–Zn1–O1 109.37(5), Cl1–Zn1–N1 112.43(5), Cl2–Zn1–O1 110.91(5), Cl2–Zn1–N1 117.97(6), O1–Zn1–N1 77.85(6), O1–H1O···Cl1 170(2), N1–C1–C6–O1 –19.8(3).

The hydrogen bonding between the OH group and one of the chloro ligands of another zinc centre leads to the formation of centrosymmetric dimers as shown in Figure 6. The distance Zn–Cl1 is about 3 pm longer than Zn–Cl2 as a result of the hydrogen bond. The H1O···Cl1 distance (2.286 Å) and the angle O1–H1O···Cl1 (170.5°) are typical for weak to moderate hydrogen bonds.[12] To the best of our knowledge, compound **8** is the first example of a structurally characterized tetrahedrally coordinated zinc complex of the type $ZnCl_2(N\cdots OH)$ in which an amino alcohol (N···OH) acts as a chelating ligand, although there is one example of a zinc compound with 2-(2-hydroxyethylamino)-6-benzylamino-9-methylpurine in a bridging coordination mode leading to a coordination polymer,[23] and some examples of five- and six-coordinate zinc dichloride complexes with amino alcohols.[24] Steric reasons could account for this behaviour; the two methyl groups at the 2-hydroxy-2-propyl moiety and the $N–CH_3$ group of a second amino alcohol will interfere with each other in a zinc complex of the type $ZnCl_2(N\cdots OH)_2$.

Spectroscopy

Although NMR spectroscopic data could only be obtained for ligand **3**, the palladium complex **4** and the zinc complex **8**, since the copper, cobalt and nickel complexes **5**–**7** are paramagnetic, the comparison of their data allows some correlations with the steric and electronic situation of the *N*,*O*-donor under different environments. Table 1 summarises the ^{1}H and ^{13}C NMR resonances of these species according to the rules of nomenclature.

Table 1. NMR spectroscopic data (^{1}H und ^{13}C[a] NMR δ values, ppm) of compounds **3**, **4** and **8**.



3

		H4		NCH_3	5-CH_3	COH	$C(CH_3)_2$
3		5.83		3.60	2.12	3.44	1.43
4		5.94		4.66	2.28	4.04	1.78
8		5.96		3.89	2.32	6.10	1.73
	C3	C4	C5	NCH_3	5-CH_3	COH	$C(CH_3)_2$
3	158.2	101.1	139.0	35.6	30.4	69.1	11.0
4	158.9	105.4	143.4	38.5	31.4	69.4	12.3
8	156.5	101.7	144.3	36.4	30.6	75.4	11.5

[a] Measured in $CDCl_3$ at room temperature.

As expected, the differences in the ^{13}C NMR chemical shifts are small and not of significance. The behaviour of the ^{1}H NMR chemical shifts between the compounds, however, varies greatly. Whereas the resonance of the proton at C4 is almost unaffected by the chemical environment of the pyrazole moiety, there is a general trend towards lower field for the resonances of the complexes compared with the free ligand. For the palladium complex **4**, the resonance of the NCH_3 group is observed at δ = 4.66 ppm, indicating an interaction of this methyl group with the empty d-orbital of the 16VE palladium site. This interaction is probably enhanced by the intramolecular Cl···HO hydrogen bond fixing the pyrazole moiety in a position almost perpendicular to the N_2Cl_2-plane. Following the order **3**, **4**, and **8**, the OH group switches from an intermolecular proton donor (δ = 3.44 ppm) to an intramolecular one (δ = 4.04 ppm) and ends up in a combination of an intermolecular proton donor site and an O–M donor (δ = 6.10 ppm), which correlates well with the chemical shift of the OH proton.

The OH absorptions of the coordinated pyrazolyl alcohol ligands in different chemical environments, measured in CH_3CN solution do not differ distinctively in their energies (see the Exp. Section). The free ligand shows an absorption (3526 cm^{-1}) that is shifted slightly (by 14–18 cm^{-1}) towards lower wavenumbers compared with the coordinated systems.

Conclusion

The ligand 2-[(1,5-dimethyl)pyrazol-3-yl]propan-2-ol turned out to be an easily accessible *N*,*O*-chelate for a series of transition metal ions. Depending on the metal site and its ligand environment, the OH group can undergo intra- or intermolecular hydrogen bonding. For six-coordinate metal sites, the facial arrangement of the three *N*-donors leads to a facial arrangement of the OH groups, which are in an ideal situation for cooperatively binding small tetrahedral anions by O–H···X interactions.

Experimental Section

General: All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Elemental analyses were carried out at the Department of Chemistry (TU Kaiserslautern). Infrared spectra were recorded with a Jasco FT-IR spectrometer. NMR spectra were recorded with a Bruker DPX 400 and a Bruker Avance 600 spectrometer.

Ethyl 1,5-Dimethylpyrazole-3-carboxylate (2): A solution of **1** (2.80 g, 18.2 mmol) in dry THF (80 mL) was slowly treated with NaH (440 mg, 18.2 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 10 min until hydrogen evolution ceased. CH_3I (1.13 mL, 18.2 mmol) dissolved in dry THF (60 mL) was added dropwise and the resulting mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo and an aqueous solution of $NaHCO_3$ (50 mL, 1 M) was added to the residue. The solution was extracted three times with Et_2O (50 mL), the organic phases were combined, dried with Na_2SO_4, and the solvent was evaporated; yield 2.70 g (89 %), yellow liquid. All spectroscopic data were in accordance with the data published in the literature.[8,9]

2-[(1,5-Dimethyl)pyrazol-3-yl]propan-2-ol (3): A solution of **2** (2.70 g, 16.1 mmol) in dry THF (20 mL) was slowly treated with a solution of MeMgCl (20 mL, 3 M) in THF. The resulting mixture was refluxed for 16 h. After cooling to room temperature a saturated solution of NH_4Cl (50 mL) was added to the yellow suspension, which was then was extracted three times with Et_2O (50 mL). The combined organic layers were dried with Na_2SO_4 and the solvent was removed. This procedure was repeated a second time. The crude product was purified by sublimation under reduced pressure; yield 1.69 g (68%), colourless prisms. $C_8H_{14}N_2O$ (154.21): calcd. C 62.31, H 9.15, N 18.17; found C 62.16, H 9.06, N 17.97. IR (KBr): $\tilde{\nu}$ = 3353 (vs, OH), 2968 (vs), 2930 (s), 1676 (s), 1551 (s), 1449 (s), 1424 (s), 1374 (vs), 1360 (vs), 1217 (vs), 1175 (vs), 1145 (vs), 1009 (m), 954 (vs), 856 (s), 827 (vs), 649 (vs), 632 (s), 595 (s) cm^{-1}. IR (CH_3CN): $\tilde{\nu}$ = 3526 (vs, OH) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 5.83 (s, 1 H, H4), 3.60 (s, 3 H, NCH_3), 2.95 (br., 1 H, OH), 2.12 (s, 3 H, CH_3), 1.43 [s, 6 H, $C(OH)(CH_3)_2$] ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.1 (C-3), 139.0 (C-5), 101.1 (C-4), 69.1 (COH), 35.6 (NCH_3), 30.4 (5-CH_3), 11.0 [$C(CH_3)_2$] ppm.

***trans*-Dichlorido{bis[2-(1,5-dimethylpyrazol-3-yl)propan-2-ol]}-palladium(II) (4):** A solution of **3** (78 mg, 0.50 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $(PhCN)_2PdCl_2$ (95.8 mg, 0.25 mmol) in CH_2Cl_2 (5 mL). The resulting red-brown solution was stirred for 2 h at room temperature, after which the colour changed to yellow. The solvent was reduced to 5 mL, Et_2O (20 mL) was added and the resulting precipitate was collected by filtration. After washing twice with Et_2O (10 mL) the product was dried in vacuo to obtain a yellow solid. Slow diffusion of Et_2O into a solution of **4** in chloroform afforded yellow crystals; yield 76.3 mg (33%). $C_{16}H_{28}Cl_2N_4O_2Pd$ (485.75): calcd. C 39.56, H 5.81, N 11.53; found C 39.55, H 5.86, N 11.56. IR (KBr): $\tilde{\nu}$ = 3468 (vs, OH), 3134 (s), 2984 (vs), 2972 (vs), 2943 (s), 2927 (s), 1557 (vs), 1439 (vs), 1426 (vs), 1392 (vs), 1363 (vs), 1334 (s), 1211 (vs), 1193 (vs), 1141 (vs), 965 (vs), 865 (m), 810 (vs), 720 (m) cm^{-1}. IR (CH_3CN): $\tilde{\nu}$ = 3628 (vs, ν_a OH), 3544 (vs, ν_s OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.94 (s, 1 H, H4), 4.67 (s, 3 H, NCH_3), 4.04 (br., 1 H, OH), 2.28 (s, 3 H, Me_{pz}), 1.78 [s, 6 H, $C(OH)(CH_3)_2$] ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.9 (C-3), 143.4 (C-5), 105.4 (C-4), 69.4 (COH), 38.5 (NCH_3), 31.4 (5-CH_3), 12.3 [$C(CH_3)_2$] ppm.

Chlorido{bis[2-(1,5-dimethylpyrazol-3-yl)propan-2-ol]}copper(II) Chloride (5): A solution of **3** (78 mg, 0.50 mmol) in acetone (10 mL) was added to a solution of $CuCl_2$ (33.6 mg, 0.25 mmol) in acetone (5 mL). The resulting red-brown solution was stirred for 4 h at room temperature, after which time the colour changed to green. The solvent was removed and the residue redissolved in $CHCl_3$ (10 mL). Slow diffusion of Et_2O into this solution afforded compound **5** as green crystals; yield 84 mg (76%). $C_{16}H_{28}Cl_2CuN_4O_2$ (442.87): calcd. C 43.39, H 6.37, N 12.65; found C 43.42, H 6.33, N 12.63. IR (KBr): $\tilde{\nu}$ = 3445 (m, OH), 3131 (s), 2974 (vs), 2851 (s), 2706 (m), 1556 (s), 1436 (s), 1391 (vs), 1363 (vs), 1308 (s), 1207 (s), 1176 (vs), 1127 (vs), 1028 (s), 956 (s), 867 (s), 820 (s), 768 (m), 661 (m) cm^{-1}. IR (CH_3CN): $\tilde{\nu}$ = 3628 (vs, ν_a OH), 3540 (vs, ν_s OH) cm^{-1}.

***fac*-Tris[2-(1,5-dimethylpyrazol-3-yl)propan-2-ol]cobalt(II) Tetrachlorocobaltate (6):** A solution of **3** (78 mg, 0.50 mmol) in methanol (10 mL) was added to a solution of $CoCl_2\cdot 6H_2O$ (59.5 mg, 0.25 mmol) in methanol (5 mL). The resulting pink solution was stirred for 4 h at room temperature. The solvent was reduced to 10 mL. Slow diffusion of Et_2O into this solution afforded **6** as blue crystals; yield 157 mg (87%). $C_{24}H_{42}Cl_4Co_2N_6O_3$ (722.31): calcd. C 39.91, H 5.86, N 11.63; found C 39.35, H 5.65, N 11.44. IR (KBr): $\tilde{\nu}$ = 3221 (vs, OH), 2977 (vs), 2695 (m), 1631 (m), 1556 (vs), 1497 (m), 1444 (s), 1385 (vs), 1352 (vs), 1289 (vs), 1205 (vs), 1177 (vs), 1119 (vs), 1018 (vs), 951 (s), 859 (s), 815 (s), 762 (m), 653 (m), 573 (m), 481 (m), 435 (m) cm^{-1}. IR (CH_3CN): $\tilde{\nu}$ = 3626 (vs, ν_a OH), 3540 (vs, ν_s OH) cm^{-1}.

***fac*-Tris[2-(1,5-dimethylpyrazol-3-yl)propan-2-ol]nickel(II) Tetrachloronickelate (7):** A solution of **3** (78 mg, 0.50 mmol) in methanol (10 mL) was added to a solution of $NiCl_2\cdot 6H_2O$ (59.4 mg, 0.25 mmol) in methanol (5 mL). The resulting green solution was stirred for 4 h at room temperature. Then the solvent was reduced to 10 mL. Slow diffusion of Et_2O into this solution afforded **7** as green crystals; yield 114 mg (63%). $C_{24}H_{42}Cl_4N_6Ni_2O_3$ (721.83): calcd. C 39.93, H 5.86, N 11.64; found C 39.57, H 6.02, N 11.50. IR (KBr): $\tilde{\nu}$ = 3392 (vs), 3229 (vs), 1626 (s), 1557 (s), 1444 (s), 1386 (s), 1293 (s), 1174 (s), 1119 (s), 1019 (s), 951 (m), 861 (s), 816 (m), 764 (m), 655 (m) cm^{-1}. IR (CH_3CN): $\tilde{\nu}$ = 3625 (vs, ν_a OH), 3540 (vs, ν_s OH) cm^{-1}.

Dichlorido[2-(1,5-dimethylpyrazol-3-yl)propan-2-ol]zinc(II) (8): A solution of **3** (78 mg, 0.50 mmol) in acetone (10 mL) was added to a solution of $ZnCl_2$ (34.1 mg, 0.25 mmol) in acetone (5 mL). The resulting colourless solution was stirred for 4 h at room temperature. The solvent was removed and the residue was redissolved in $CH_2Cl_2/CHCl_3$ (1:1; 10 mL). Slow diffusion of Et_2O into this solution afforded **8** as colourless crystals; yield 67 mg (92%). $C_8H_{14}Cl_2N_2OZn$ (290.53): calcd. C 33.07, H 4.86, N 9.64; found C 33.22, H 4.89, N 9.69. IR (KBr): $\tilde{\nu}$ = 3273 (vs, OH), 2978 (s), 1627 (w), 1552 (vs), 1439 (s), 1386 (vs), 1303 (vs), 1295 (s), 1168 (vs), 1119 (vs), 1027 (s), 948 (m), 857 (vs), 817 (vs), 657 (m), 485 (w) cm^{-1}. IR (CH_3CN): $\tilde{\nu}$ = 3628 (vs, ν_a OH), 3544 (vs, ν_s OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.10 (br., 1 H, OH), 5.96 (s, 1 H, H4), 3.88 (s, 3 H, NCH_3), 2.32 (s, 3 H, 5-CH_3), 1.73 [s, 6 H, $C(OH)(CH_3)_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5 (s, C3), 144.3 (s, C5), 101.7 (C4), 75.4 (s, COH), 36.4 (s, NCH_3), 30.6 (s, 5-CH_3), 11.5 [s, $C(OH)(CH_3)_2$] ppm.

Magnetic Measurements: Magnetic susceptibility data (1.8–300 K) were collected on powdered samples using SQUID magnetometer on Quantum Design model MPMS-XL instrument under a 0.1 T applied magnetic field. The magnetization isotherm was collected between 0 and 7 T at 2, 3 and 5 K. All data were corrected for the contribution of the sample holder.

X-ray Structure Analyses: Crystal data and refinement parameters (Oxford Diffraction Gemini) for compounds **3**–**8** are collected in Table 2. The structures were solved by direct methods (SIR92[25]), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.[26] Semi-empirical absorption corrections from equivalents (Multiscan) were carried out.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms positions were calculated in ideal positions (riding model) except for the hydrogen atoms H1O and H2O bound to oxygen atoms O1 and O2, respectively, in **5**, the hydrogen atoms H1O, H2O and H3O bound to oxygen atoms O1, O2 and O3, respectively, in **6**, the hydrogen atoms H1O, H2O and H3O bound to oxygen atoms O1, O2 and O3, respectively, in **7** and the hydrogen atom H1O bound to oxygen atom O1 in **8**, which were located in the difference Fourier synthesis. Each of these hydrogen atoms were then refined semi-freely with the help of a distance restraint, while constraining its U value to 1.5 times the U_{eq} value of the bonded oxygen atom.

CCDC-812629 (for **3**), -812630 (for **4**), -812625 (for **5**), -812628 (for **6**), -812627 (for **7**) and -812626 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): IR and NMR spectra.

Table 2. Summary of the crystallographic data and details of data collection and refinement for compounds **3**–**8**.

	3	**4**	**5**	**6**	**7**	**8**
Empirical formula	$C_8H_{14}N_2O$	$C_{16}H_{28}Cl_2N_4O_2Pd$	$C_{16}H_{28}Cl_2CuN_4O_2$	$C_{24}H_{42}Cl_4Co_2N_6O_3$	$C_{24}H_{42}Cl_4N_6Ni_2O_3$	$C_8H_{14}Cl_2N_2OZn$
Formula weight	154.21	485.72	442.86	722.30	721.86	290.48
Crystal size [mm]	0.33 × 0.11 × 0.08	0.18 × 0.17 × 0.09	0.24 × 0.20 × 0.20	0.04 × 0.04 × 0.02	0.08 × 0.07 × 0.06	0.20 × 0.12 × 0.10
T [K]	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
λ [Å]	0.71073	0.71073	1.54184	1.54184	1.54184	1.54184
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$C2/c$	$Pna2_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	9.6037(2)	15.6854(6)	15.8306(2)	16.6076(5)	16.4985(6)	10.2664(2)
b [Å]	11.6264(3)	9.3308(2)	11.58740(10)	12.2490(3)	12.2317(3)	7.86270(10)
c [Å]	7.7550(2)	16.1203(6)	11.89110(10)	17.1278(5)	17.0830(5)	16.1469(2)
α [°]	90	90	90	90	90	90
β [°]	90	117.310(3)	90	110.980(4)	110.714(4)	106.062(2)
γ [°]	90	90	90	90	90	90
V [Å^3]	865.90(4)	2096.35(12)	2181.25(4)	3253.26(18)	3224.58(19)	1252.52(4)
Z	4	4	4	4	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.183	1.539	1.349	1.475	1.487	1.540
μ [mm^{-1}]	0.080	1.156	3.797	11.299	4.790	6.434
θ range [°]	2.75–32.35	2.92–32.42	4.73–62.65	4.55–64.84	4.55–62.92	6.21–62.62
Reflections coll.	11229	14614	15668	16134	16524	10994
Indep. reflections	1579 (R_{int} = 0.0451)	3527 (R_{int} = 0.0306)	3244 (R_{int} = 0.0372)	5103 (R_{int} = 0.0665)	5054 (R_{int} = 0.0532)	1987 (R_{int} = 0.0338)
Data/restr./param.	1579/1/105	3527/0/120	3244/3/241	5103/3/373	5054/3/373	1987/1/134
Final R indices [$I > 2\sigma(I)$][a]	0.0403, 0.0956	0.0205, 0.0475	0.0263, 0.0650	0.0323, 0.0535	0.0320, 0.0599	0.0220, 0.0543
R (all data)[b]	0.0575, 0.1034	0.0302, 0.0490	0.0288, 0.0655	0.0767, 0.0638	0.0650, 0.0663	0.0270, 0.0551
GooF[c]	1.023	0.973	1.031	0.833	0.820	0.970
Flack parameter	10(10)[d]	–	0.475(15)	–	–	–
$\Delta\rho_{max/min}$ [e Å^{-3}]	0.259/–0.239	0.630/–0.445	0.526/–0.252	0.376/–0.395	0.262/–0.264	0.273/–0.298

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$. [c] $GooF = [\Sigma w(F_o^2 - F_c^2/n - p)]^{1/2}$. [d] During the refinement MERG 4 was used.

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft (DFG) for financial support of this work.

---

[1] a) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, John Wiley & Sons, New York, **1994**; b) R. Noyori, M. Kitamura, *Angew. Chem.* **1991**, *103*, 34–55; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 49–69; c) N. Bellocq, S. Abramson, M. Lasperas, D. Brunel, P. Moreau, *Tetrahedron: Asymmetry* **1999**, *10*, 3229–3241; d) M. Asami, H. Watanabe, K. Honda, S. Inoue, *Tetrahedron: Asymmetry* **1998**, *9*, 4165–4173; e) J. Wilken, M. Kossenjans, H. Gröger, J. Martens, *Tetrahedron: Asymmetry* **1997**, *8*, 2007–2015; f) C. Bolm, K. M. Fernandez, A. Seger, G. Raabe, *Synlett* **1997**, 1051–1052; g) H. Kotsuki, M. Wakao, H. Hayakawa, T. Shimanouchi, M. Shiro, *J. Org. Chem.* **1996**, *61*, 8915–8920.

[2] W. A. Herrmann, O. Runte, N. Huber, *Angew. Chem.* **1995**, *107*, 2371–2390; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2187–2206.

[3] W. R. Thiel, J. Eppinger, *Chem. Eur. J.* **1997**, *3*, 696–705.

[4] a) C. Sabate-Alduy, J. Bastide, *Bull. Soc. Chim. Fr.* **1972**, 2764–2769; b) J. Bastide, J. Lematre, *C. R. Acad. Sci. C* **1969**, *269*, 358–360.

[5] a) R. Plate, M. J. M. Plaum, R. G. A. van der Hulst, T. de Boer, *Bioorg. Med. Chem.* **2000**, *8*, 449–454; b) C. D. Jones, M. A. Winter, K. S. Hirsch, N. Stamm, H. M. Taylor, H. E. Holden, J. D. Davenport, E. V. Krumkalns, R. G. Suhr, *J. Med. Chem.* **1990**, *33*, 416–429; c) R. W. Fries, D. P. Bohlken, B. V. Plapp, *J. Med. Chem.* **1979**, *22*, 356–359.

[6] a) J. Elhaik, C. A. Kilner, M. A. Halcrow, *Cryst. Engin. Commun.* **2005**, *7*, 151–157; b) M. Kujime, S. Hikichi, M. Akita, *Chem. Lett.* **2003**, *32*, 486–487; c) N. Kitajima, M. Osawa, M. Tanaka, Y. Moro-oka, *J. Am. Chem. Soc.* **1991**, *113*, 8952–8953; d) S. Hikichi, H. Komatsuzaki, N. Kitajima, M. Akita, M. Mukai, T. Kitagawa, Y. Moro-Oka, *Inorg. Chem.* **1997**, *36*, 266–267; e) U. P. Singh, V. Aggarwal, A. K. Sharma, *Inorg. Chim. Acta* **2007**, *360*, 3226–3232; f) S. Hikichi, H. Komatsuzaki, M. Akita, Y. Moro-oka, *J. Am. Chem. Soc.* **1998**, *120*, 4699–4710.

[7] M. Dewar, F. King, *J. Chem. Soc.* **1945**, 114–116.

[8] a) A. Schmidt, T. Habeck, M. Kindermann, M. Niegler, *J. Org. Chem.* **2003**, *68*, 5977–5982; b) H. v. Auwers, H. Hollmann, *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 1282–1302.

[9] T. Persson, J. Nielsen, *Org. Lett.* **2006**, *8*, 3219–3222.

[10] a) W. Thiel, M. Angstl, T. Priermeier, *Chem. Ber.* **1994**, *127*, 2373–2379; b) W. Thiel, T. Priermeier, *Angew. Chem.* **1995**, *107*, 1870–1871; W. Thiel, T. Priermeier, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1737–1738; c) K. Rößler, T. Kluge, A. Schubert, Y. Sun, E. Herdtweck, W. R. Thiel, *Z. Naturforsch., Teil B* **2004**, *59*, 1253–1264.

[11] C. Seubert, Y. Sun, W. Thiel, *Dalton Trans.* **2009**, 4971–4977.

[12] T. Steiner, *Angew. Chem.* **2002**, *114*, 50–80; T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76.

[13] a) A. Godoy Netto, A. Mauro, R. Frem, A. Santana, R. Santos, J. Zoia, *J. Coord. Chem.* **2001**, *54*, 129–141; b) A. Boixassa, J. Pons, A. Virgili, X. Solans, M. Font-Bardia, J. Ros, *Inorg. Chim. Acta* **2002**, *340*, 49–55; c) A. Boixassa, J. Pons, X. Solans, M. Font-Bardia, J. Ros, *Chim. Acta* **2004**, *357*, 733–738; d) V. Montoya, J. Pons, X. Solans, M. Font-Bardia, J. Ros, *Inorg. Chim. Acta* **2005**, *358*, 2312–2318.

[14] a) A. Pañella, J. Pons, J. García-Antón, X. Solans, M. Font-Bardia, J. Ros, *Inorg. Chim. Acta* **2006**, *359*, 4477–4482; b) S. Scheuermann, T. Kretz, H. Vitze, J. Bats, M. Bolte, H. Lerner, M. Wagner, *Chem. Eur. J.* **2008**, *14*, 2590–2601.

[15] M. Barz, E. Herdtweck, W. Thiel, *Polyhedron* **1998**, *17*, 1121–1131.

[16] a) S. Telfer, N. Parker, R. Kuroda, T. Harada, J. Lefebvre, D. Leznoff, *Inorg. Chem.* **2008**, *47*, 209–218; b) B. Antonioli, D.

Bray, J. Clegg, K. Jolliffe, K. Gloe, K. Gloe, L. Lindoy, *Polyhedron* **2007**, *26*, 673–678; c) S. Hamamci, V. Yilmaz, C. Thöne, *Acta Crystallogr., Sect. E. Struct. Rep. Online* **2004**, *60*, m159–m161.

[17] a) M. Gennari, M. Tegoni, M. Lafranchi, M. Pellinghelli, L. Marchiò, *Inorg. Chem.* **2007**, *46*, 3367–3377; b) L. Ballester, A. Gil, A. Gutiérrez, M. Perpiñán, M. Azcondo, A. Sánchez, C. Marzin, G. Tarrago, C. Bellitto, *Chem. Eur. J.* **2002**, *8*, 2539–2548.

[18] S. Bergner, G. Wolmershäuser, H. Kelm, W. R. Thiel, *Inorg. Chim. Acta* **2008**, *361*, 2059–2069.

[19] a) T. B. Vancejun, E. M. Holt, C. G. Pierpont, S. L. Holt, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *36*, 150–153; b) D. M. L. Goodgame, D. A. Grachvogel, I. Hussain, A. J. P. White, D. J. Williams, *Inorg. Chem.* **1999**, *38*, 2057–2063; c) B. B. Miminoshvili, A. E. Shvelashvili, T. O. Vardosanidze, *Russ. J. Inorg. Chem.* **1996**, *41*, 2066; d) P. Jaitner, K. Wurst, *Inorg. Chim. Acta* **1997**, *255*, 95–98.

[20] Search in the Cambridge Crystallographic Database, version 5.31 (November **2009**).

[21] a) C. J. Boxwell, P. H. Walton, *Chem. Commun.* **1999**, 1647–1648; b) A. A. Belal, L. J. Farrugia, R. D. Peacock, J. Robb, *J. Chem. Soc., Dalton Trans.* **1989**, 931–935; c) X.-M. Feng, Z. Zhang, Y.-Z. Li, N.-S. Bian, Z.-L. Wang, *Trans. Met. Chem.* **2007**, *32*, 95–101; d) H. Al-Sagher, I. Fallis, L. J. Farrugia, R. D. Peacock, *J. Chem. Soc., Chem. Commun.* **1993**, 1499–1500; e) L. Cronin, B. Greener, M. H. Moore, P. H. Walton, *J. Chem. Soc., Dalton Trans.* **1996**, 3337–3339; f) V. T. Yilmaz, O. Andac, A. Karadag, W. T. A. Harrison, *J. Mol. Struct.* **2002**, *641*, 119–124; g) I. A. Fallis, L. J. Farrugia, N. M. Macdonald, R. D. Peacock, *J. Chem. Soc., Dalton Trans.* **1993**, 2759–2763; h) G. T. Smith, P. R. Mallinson, R. D. Peacock, L. J. Farrugia, I. A. Fallis, C. S. Frampton, J. A. K. Howard, *Chem. Commun.* **1996**, 525–532; i) G. T. Smith, P. R. Mallinson, C. S. Frampton, L. J. Farrugia, R. D. Peacock, J. A. K. Howard, *J. Am. Chem. Soc.* **1997**, *119*, 5028–5034; j) T. Tanase, H. Inukai, T. Onaka, M. Kato, S. Yano, S. J. Lippard, *Inorg. Chem.* **2001**, *40*, 3943–3953.

[22] a) L. Alagna, S. S. Hasnain, B. Piggott, D. J. Williams, *Biochem. J.* **1984**, *220*, 591–595; b) H. Kiriyama, T. Fukuda, Y. Yamagata, E. Sekido, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 1441–1444; c) A. Yuchi, H. Murakami, M. Shiro, H. Wada, G. Nakagawa, *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3362–3373; d) A. Kermagoret, P. Braunstein, *Dalton Trans.* **2008**, 1564–1573.

[23] Z. Travnicek, V. Krystof, M. Sipl, *J. Inorg. Biochem.* **2006**, *100*, 214–225.

[24] a) S. Loukiala, J. Ratilainen, K. Airola, J. Valkonen, K. Rissanen, *Acta Chem. Scand.* **1998**, *52*, 593–602; b) X.-X. Sun, C.-M. Qi, S.-L. Ma, H.-B. Huang, W.-X. Zhu, Y.-C. Liu, *Inorg. Chem. Commun.* **2006**, *9*, 911–914; c) M. Tesmer, B. Müller, H. Vahrenkamp, *Chem. Commun.* **1997**, 721–722; d) A. Visnjevac, L. Tusek-Bozic, M. Majeric-Elenkov, Z. Hamersak, H. Kooijman, E. De Clercq, B. Kojic-Prodic, *Polyhedron* **2002**, *21*, 2567–2577.

[25] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435–435.

[26] G. M. Sheldrick, *SHELX-97: Programs for Crystal Structure Analysis*, University of Göttingen, Göttingen, Germany, **1998**.

[27] *CrysAlis Red*, Oxford Diffraction Ltd., version 1.171.32.5, **2007**.

Received: November 23, 2010