Highly Substituted Tris(pyrazolyl)methane Ligands and Some Zinc Complexes Thereof

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Received July 17, 1995

Key Words: Zinc complexes / Tridentate ligands / Tris(pyrazolyl)methane / Reactivity / Structure

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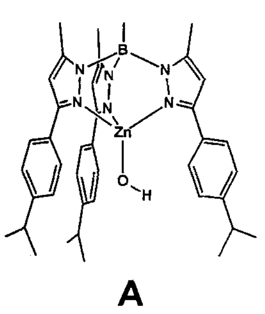
Tris(pyrazolyl)methane ligands in which two or three of the pyrazole carbon atoms bear organic substituents ($\mathbf{L}^1-\mathbf{L}^7$) were synthesized from chloroform and the corresponding pyrazole under phase transfer conditions. Their behavior towards zinc salts was found to span the range from no reaction at all to hydrolytic destruction. One hydrolysis product isolated and structurally characterized was the perchlorate complex $[(HPz^5)_3Zn-OClO_3]ClO_4$ (**1**), other ones were the 2:1 complexes $(HPz^3)_2ZnBr_2$ (**2**) and $(HPz^6)_2Zn(NO_3)_2$ (**3**, HPz^n = substituted pyrazole). Zinc perchlorate and tris(trimethylpyrazolyl)methane ($\mathbf{L}^2$) formed the octahedral binary complex $[\mathbf{L}^2_2Zn](ClO_4)_2$ (**4**) as evidenced by a structure determination. Zinc halides produced the 1:1 complexes $\mathbf{L}^1 \cdot ZnBr_2$ (**5**), $\mathbf{L}^4 \cdot ZnCl_2$ (**6**), and $\mathbf{L}^4 \cdot ZnBr_2$ (**7**), which according to the structure determinations of **6** and **7** contain tetrahedral ZnN_2Hal_2 units with only bidentate tris(pyrazolyl)methane ligands. In contrast, the zinc nitrate complex $\mathbf{L}^4 \cdot Zn(NO_3)_2$ (**8**) was found to have an octahedral structure with mono- and bidentate nitrate and tridentate L^4. The bromide complex **7** was converted by silver perchlorate hydrate into the labile compound $[\mathbf{L}^4 \cdot ZnBr]ClO_4$ (**9**) and then into the unstable product $[\mathbf{L}^4 \cdot Zn-OH_2](ClO_4)_2$ (**10**), both presumed to contain zinc in a tetrahedral ZnN_3Br or ZnN_3O environment, respectively. The ease of hydrolytic self-destruction prevented the exploitation of the reactivity of **9** and **10** in analogy to that of the corresponding tris(pyrazolyl)borate zinc complexes.

The coordination chemistry of zinc suffers from lability and low thermodynamic stabilities. As a result it is difficult to gain a reliable control over the access to or reactivity at specific coordination sites. One approach to reduce these problems consists of the use of encapsulating ligands. These types of ligands, typically tripodal chelators, have the property of occupying all but one or two of the coordination sites around the metal. Thus, the thermodynamic stability of the complexes is enhanced due to the chelate effect, and their reactivity is reduced to the functionality of the remaining coordination sites.

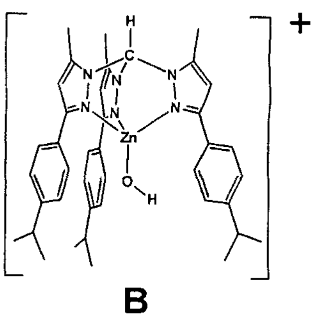
Only a limited number of tripodal ligands has been used so far with the purpose of studying zinc complex reactivities, mostly with a view to modelling zinc-containing enzymes. Among them are tris(imidazolyl)phosphanes[1], tris(imidazolyl)methanols[2], tris(pyridylmethyl)amines[3], bis(aminoethyl)glycine[4], and bis(mercaptoethyl)pyridines[5]. We contributed studies with tris(aminomethyl)ethane[6], cyclohexanetriamines[7], tris(pyridyl)phosphane[8], and tris(imidazolylmethyl)amines[9]. The most productive tripod ligands for zinc enzyme modelling, in our[10,11] as well as in other hands[12], have been the tris(pyrazolyl)borates. The reason for their superior usability is the fact that their encapsulating properties can be enhanced by voluminous substituents in the 3- and 5-positions of the pyrazole rings.

In order to exploit these favorable properties with uncharged ligands we set out to prepare and use some highly substituted tris(pyrazolyl)methane derivatives which are isoelectronic with the corresponding tris(pyrazolyl)borates. Except for the methyl-substituted compounds $\mathbf{L}^1$[13] and $\mathbf{L}^2$[14] (see below) no such compounds were described in the literature. Furthermore, in contrast to the coordination chemistry of tris(pyrazolyl)borates that of tris(pyrazolyl)methanes is rather underdeveloped and mostly limited to some organometallic compounds[13,15,16]. To our knowledge the zinc complex chemistry of tris(pyrazolyl)methanes was until now limited to the preparation and structure determination of the 2:1 complex of the unsubstituted parent ligand, $[(HCPz_3)_2Zn](NO_3)_2$[17].

A main goal of the work described here was the synthesis of tetrahedral complexes L_3Zn-X in which the three L positions are occupied by the tris(pyrazolyl)methane ligand and in which the ligand X can be varied by chemical transformations. The preferred ligand X was a water molecule or an OH group as exemplified by the isoelectronic pair of complexes **A** and **B**. It was hoped that just like the enzyme model **A**[11] complexes like **B** could be used for hydrolytic interconversions of biorelevant substrates.



A



B

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The Pyrazolylmethane Ligands

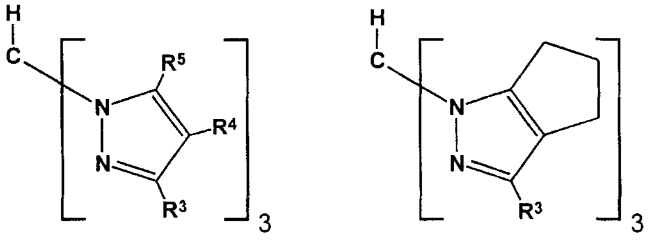
Tris(pyrazolyl)methanes are tris-amides of orthocarbonic acid. As such they are sensitive towards hydrolysis, and their synthesis from trifunctional methane derivatives may result in low yields. We chose to prepare them from chloroform and the corresponding pyrazoles **HPz**^{n}. Of the two reported procedures to do this, the potassium-pyrazolate method[18] and the phase-transfer method[19], we opted for the latter. It involves the reaction between chloroform and the pyrazole **HPz**^{n} in benzene in the presence of the phase-transfer catalyst, using a concentrated aqueous solution of NaOH as the base. The yields of this reaction are only moderate; they depend critically on the right choice of reaction temperature and time, and the workup procedure can be cumbersome. According to our experience, however, the overall effort for this method of synthesis is less than for the other methods.

pyrazoles HPz^n

	R^3	R^4	R^5
HPz^1	Me	H	Me
HPz^2	Me	Me	Me
HPz^3	t-Bu	H	Me

	R^3
HPz^4	i-Pr
HPz^5	t-Bu
HPz^6	Ph
HPz^7	i-Pr-Ph

tris(pyrazolyl)methane ligands L^n



	R^3	R^4	R^5
L^1	Me	H	Me
L^2	Me	Me	Me
L^3	t-Bu	H	Me

	R^3
L^4	i-Pr
L^5	t-Bu
L^6	Ph
L^7	i-Pr-Ph

We used the synthetic method for the preparation of the two methyl-substituted tris(pyrazolyl)-methanes L^1[13] and L^2[14] which we obtained in 24 and 31% yield, respectively. We then used it for the preparation of L^3 expecting that the *tert*-butyl substituents in the 3-positions of the pyrazole rings would provide the favourable hydrophobic pocket around the zinc ion in complexes of L^3 just as they do in zinc complexes of the corresponding tris(pyrazolyl)-borate[10]. The yield of L^3 (7%) was disappointingly low, and side reactions prevailed. This points to the general weakness of $CHCl_3$ reactions in the presence of NaOH, the formation of dichlorocarbene. As long as the reacting pyrazole bears only one or two substituents at its carbon atoms the likelihood of CCl_2 attack at the unsubstituted positions is high, lowering the chance of a successful three-step substitution on $CHCl_3$ by the pyrazole.

We therefore resorted to a type of pyrazoles which are fully substituted, bearing an annelated cyclopentane ring to occupy the 4- and 5-positions of the pyrazole ring and having a variable and voluminous substituent in the 3-position. This latter substituent was again chosen by analogy with the corresponding pyrazolylborates[10–12] with the purpose of controlling the steric and electronic environment of a coordinated zinc ion. Thus, with the corresponding pyrazoles bearing aliphatic substituents the ligands L^4 and L^5 were obtained in 45 and 24% yield, respectively. Aromatic substitution was achieved with phenyl and *p*-cumyl groups in the 3-position, leading to ligands L^6 and L^7 in 26 and 27% yield, respectively. Ligand L^7 represents the closest approach to the ligand systems depicted in formulas **A** and **B**.

The IR spectra of the ligands L^n (see Table 1) lack a typical feature like the ν(BH) band of the tris(pyrazolyl)-borates. They do show strong ring vibration bands, the most prominent of which is listed in the table. The methyne CH function still provides the most characteristic spectroscopic feature of the ligands by its isolated resonance in the ^{1}H- as well as in the ^{13}C-NMR spectra (see Table 1). Further spectral data are given in the experimental part. Ligand L^7 of which no zinc complexes could be obtained (see below) was subjected to an EI-MS measurement, producing with low intensity the molar mass peak at *m/z* = 688.4.

Table 1. Characteristic features in the spectra of the tris(pyrazolyl)-methane ligands

	IR ν(ring)[a]	^{1}H-NMR δ(methyne)[b]	^{13}C-NMR δ(methyne)[b]
L^1	1569	8.00	
L^2	1588	8.00	
L^3	1555	8.00	82.0
L^4	1558	7.92	82.7
L^5	1559	7.94	82.6
L^6	1556	8.23	
L^7	1552	8.22	83.1

[a] In KBr, cm^{-1}. – [b] HCX_3 resonance, in $CDCl_3$, int. TMS.

Reaction with Zinc Salts

All seven ligands L^n were treated with zinc salts under various conditions. Zinc bromide was chosen as the zinc halide because, in contrast to zinc chloride, it is easy to obtain and handle as a water-free compound. Zinc nitrate was chosen because the nitrate anion is the most versatile in zinc complex chemistry as it behaves as a unidentate or bidentate ligand as well as a non-coordinating anion. Zinc perchlorate was chosen on the assumption that the perchlorate anion would be non-coordinating. In general, the reactions were performed in a 1:1 (zinc salt:ligand) stoichiometry with the purpose of obtaining $\mathbf{L} \cdot Zn{-}X$ complexes.

The results of the complexation reactions were quite varied and often surprising. It turned out that the tris(pyrazolyl)methanes in contrast to the tris(pyrazolyl)borates were not reliably tridentate and not reliably stable when exposed to zinc salts in the presence of ligating anions, aqua ligands, or alcohol solvents. Specifically, the hydrolytic destruction of the tris(pyrazoyl)methanes after addition of the zinc salts was a common problem. It had to be avoided by controlling the reaction temperature and time. It could not be avoided in the standard solvent methanol for ligands $\mathbf{L}^3$, $\mathbf{L}^5$, and $\mathbf{L}^6$. As a result, zinc complexes of the corresponding pyrazoles were isolated.

In the case of $\mathbf{L}^5$ the ligand hydrolysis produced one of the surprises of this work as it led to the perchlorate complex **1**. The hydrolysis reaction seems to consume the coordinated water of the reagent $[Zn(H_2O)_6](ClO_4)_2$, leaving only zinc ions, pyrazole, and perchlorate ions in solution. While one would expect the compound $[Zn(\mathbf{HPz}^5)_4](ClO_4)_2$ to crystallize from this solution, the isolated complex **1** seems to be preferred despite the unusual zinc-perchlorate ligation, due to the 3:1 (ligand:zinc) composition of the solution and its preferred crystallization.

1 $[(\mathbf{HPz}^5)_3Zn{-}OClO_3]ClO_4$

The hydrolysis of $\mathbf{L}^3$ in the presence of $ZnBr_2$ and that of $\mathbf{L}^6$ in the presence of $Zn(NO_3)_2$ produced pyrazole complexes of no unusual composition. The anions present have ligating properties, and based on the expectation that tetrahedral zinc complexes will be formed the resulting $\mathbf{L}^2ZnX_2$ complexes **2** and **3** are the "natural" result as neutral molecular species.

$(\mathbf{Hpz}^3)_2ZnBr_2$ $(\mathbf{HPz}^6)_2Zn(NO_3)_2$
2 **3**

Only in one case was an octahedral bis(ligand) complex isolated. While this was not to be expected for the bulky ligands $\mathbf{L}^4-\mathbf{L}^7$ it had to be taken into consideration for $\mathbf{L}^1-\mathbf{L}^3$, and it was realized for $\mathbf{L}^2$. The resulting complex **4** was the only isolable product of reactions between $\mathbf{L}^2$ and zinc salts of noncoordinating anions, irrespective of the stoichiometric ratio of the reactants.

4 $[(\mathbf{L}^2)_2Zn](ClO_4)_2$

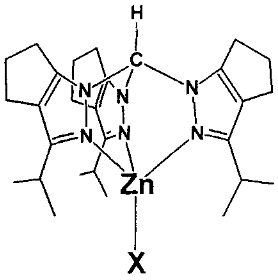
All the remaining reactions reported here led to complexes with a 1:1 ($Zn{:}\mathbf{L}^n$) composition. The structure determinations (see below) revealed, however, that this does not imply tridentate coordination of $\mathbf{L}^n$ as it always does for tris(pyrazolyl)borate-zinc complexes. Thus, the reaction of $\mathbf{L}^1$ and $\mathbf{L}^4$ with $ZnBr_2$ produced the $\mathbf{L}^nZnX_2$ complexes **5** and **7**. Complex **6** which is the chloride analogue of **7** and has the same structure (see below) was left to us by Prof. Kaim[20] for structural comparisons. Complexes **5**–**7** have the common property of being tetrahedral with a ZnN_2Hal_2 coordination, leaving one pyrazole "leg" of the tris(pyrazolyl)methane tripods uncoordinated.

$\mathbf{L}^1 \cdot ZnBr_2$ $\mathbf{L}^4 \cdot ZnCl_2$ $\mathbf{L}^4 \cdot ZnBr_2$
5 **6** **7**

The reaction between $\mathbf{L}^4$ and zinc nitrate also produced a 1:1 complex, **8**. However, this complex according to the structure determination does contain tridentate $\mathbf{L}^4$, and furthermore it is octahedral with one monodentate and one bidentate nitrate ligand. Thus, the lower ligating power of the nitrate ion towards zinc as compared with that of the halide ions is compensated by an increased hapticity of ligand $\mathbf{L}^4$ as well as by the anions.

8 $(\mathbf{L}^4)Zn(ONO_2)(O_2NO)$

In the course of these studies ligand $\mathbf{L}^4$ turned out to be the only one that can form 1:1 complexes with zinc *and* act as a tridentate ligand. Some efforts were therefore made to use it for obtaining the desired tetrahedral $\mathbf{L} \cdot Zn{-}X$ complexes of a constitution like **B**. It proved impossible to use it for a direct reaction with $Zn(ClO_4)_2 \cdot 6\ H_2O$ which in the case of the tris(pyrazolyl)borates provides access to the tetrahedral (tripod)ZnOH complexes[10,11], probably again due to partial hydrolysis of $\mathbf{L}^4$. An approach to the desired $\mathbf{L} \cdot Zn{-}X$ species could, however, be gained by anion substitution starting from complex **7**. Reaction of **7** with one equivalent of silver perchlorate hydrate afforded compound **9** which is stable enough to survive recrystallization, but not to be stored or subjected to reactions in protic solvents. Two equivalents of silver perchlorate hydrate removed both bromide ligands from **7**, generating compound **10** which contains one water molecule. Complex **10** decomposes rapidly in solution and undergoes hydrolytic destruction immediately when traces of water are present. Thus, although **10** is the closest analog of type **B** obtained here it cannot be used for chemical reactions in analogy to the chemistry of complex type **A**. As crystals of **9** and **10** suitable for a structure determination could not be obtained, their constitutional assignment as tetrahedral $\mathbf{L}^4 \cdot Zn{-}X$ complexes rests on their spectra alone.



9: X = Br **10**: X = OH_2

A final major difference between tris(pyrazolyl)borate and tris(pyrazolyl)methane zinc complexes was observed when trying to use the aryl-substituted ligands $\mathbf{L}^6$ and $\mathbf{L}^7$, whose borate analogs have provided a fertile derivative chemistry[11,21]. Ligand $\mathbf{L}^6$ was non-productive due to its very low solubility and its sensitivity towards hydrolysis. $\mathbf{L}^7$, to our surprise, did not react with any zinc salt [$ZnCl_2$, $ZnBr_2$, $Zn(OAc)_2$, and $Zn(ClO_4)_2$]. Combinations of these salts with $\mathbf{L}^7$ in different solvents invariably produced the same result, i.e. re-isolation of $\mathbf{L}^7$.

Product Identification

All complexes **1**–**10** show IR and ^{1}H-NMR spectra which are in accord with their given constitutions (for details see Experimental). Table 2 lists the characteristic features. In the IR spectra of the pyrazole complexes **1**–**3** the ν(NH) band is present, in those of the tris(pyrazolyl)-methane complexes the ring vibration band near 1560 cm^{-1} is shifted to slightly higher wavenumbers. The most typical ^{1}H-NMR signal is again the methyne singlet. The oxo anions present in **1**, **3**, **4**, **8**, **9**, and **10** produce their typical IR bands. Specifically, in **1** the coordinating (1146 and 1025 cm^{-1}) and the noncoordinating perchlorate (1094 cm^{-1}) can be distinguished. Conversely, complexes **5**–**7** containing unsymmetrically coordinated tris(pyrazolyl)methanes give rise to only one set of pyrazolyl ^{1}H-NMR resonances, thereby indicating an exchange of the coordinated and the noncoordinated pyrazole units. Taking this and the existence of the coordinated perchlorate anion in **1** into account, we must consider the constitutions assumed for **9** and **10** (with tridentate L^4 and tetrahedral geometry) with some reservation. However, the IR spectra of **9** and **10** point only to a noncoordinated perchlorate ligand, and the ^{1}H-NMR spectrum of **10** displays a signal in a reasonable range (5.8 ppm) for a zinc-bound water molecule.

Table 2. Characteristic ligand resonances in the IR and ^{1}H-NMR spectra of complexes **1**–**10**

	IR$^{a)}$	^{1}H-NMR$^{b)}$	
	ν(cm^{-1})	solvent	δ(ppm)
1	3359/3234	acetone-d$_6$	4.50
2	3135	CDCl$_3$	6.00
3	3269	-	-
4	1588	CD$_3$OD	8.17
5	1566	D$_2$O	8.18
6	1576	CDCl$_3$	7.50
7	1564	DMSO-d$_6$	7.82
8	1564	CDCl$_3$	8.29
9	1558	acetone-d$_6$	8.86
10	1562	acetone-d$_6$	8.23

$^{a)}$ ν(NH) for **1**–**3**, ν(ring) for **4**–**10**. – $^{b)}$ δ(NH) for **1**, δ(pyrazole-CH) for **2**, δ(methyne-CH) for **4**–**10**.

Most of the complex types described here were verified by structure determinations. This holds for the perchlorate complex **1** (Figure 1) whose existence could only be proven in this way. The three pyrazole ligands and the perchlorate provide a coordination which is tetrahedral to a reasonably good approximation. The Zn–N distances are normal, cf. [(methylimidazole)$_4$Zn](ClO$_4$)$_2$ (1.98–2.02 Å)[22]. The Zn–O distance is quite short when compared to that in the two other characterized zinc-perchlorate complexes [(1-aminoethyl-1,5,9-triazacyclododecane)Zn(ClO$_4$)$_2$] (2.52 Å)[23] and [(1-pyrrolidinyl-1,5,9-triazacyclododecane)Zn-(ClO$_4$)$_2$] (2.71 Å)[24]. This proves that the perchlorate ligand in **1** is not a weakly coordinated anion but a regular oxygen ligand. In the lattice of **1** both the coordinated and the noncoordinated perchlorate ions are linked by hydrogen bonds to neighbouring NH groups of the pyrazole ligands. The Cl–O distances in the two perchlorate ions show a considerable range (1.32–1.49 Å), with the coordinated Cl–O unit having the second longest bond (1.46 Å).

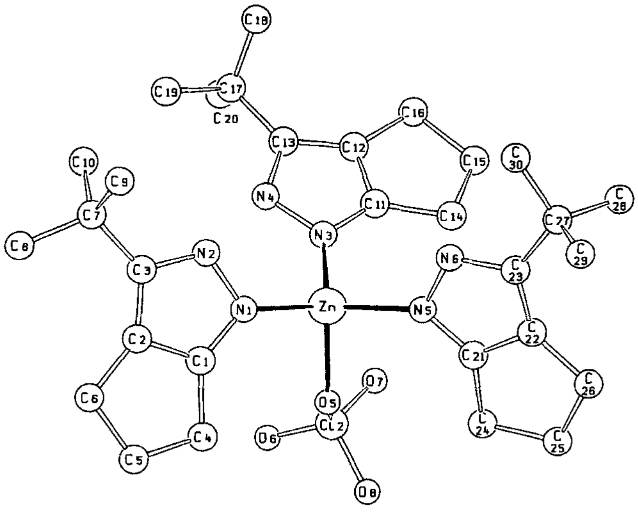


Figure 1. A view of the cation of complex **1**. Selected bond lengths [Å]: Zn–N1 1.977(4), Zn–N3 1.973(5), Zn–N5 1.997(4), Zn–O5 2.039(4). – Bond angles [°]: N1–Zn–N3 113.6(2), N1–Zn–N5 120.6(2), N1–Zn–O5 101.5(2), N3–Zn–N5 109.6(2), N3–Zn–O5 113.7(2), N5–Zn–O5 96.1(2)

The octahedral bis-ligand complex **4** (Figure 2) is ideally centrosymmetric due to the location of the zinc ion on a crystallographic inversion center. All its bonding and geometric characteristics have been observed before, viz. in the known tris(pyrazolyl)methane complex [(HCPz$_3$)$_2$Zn]-(NO$_3$)$_2$[17], in bis[tris(pyrazolyl)borate]zinc complexes[25], in bis[tris(pyridyl)phosphane]zinc perchlorate[8], and in bis-[tris(methylaminomethyl)ethane]zinc perchlorate[6]. In all these complexes the Zn–N distances are in the range of 2.15–2.20 Å, the intraligand N–Zn–N angles are around 85° and the interligand N–Zn–N angles around 95°.

For complexes **5**–**7** the ^{1}H-NMR data gave the misleading information that they might contain symmetrically tridentate L^1 and L^4 which would imply that one of their halide ions was coordinated like in [L^n·Zn–Hal]Hal. The structure determinations of **6** and **7**, of which that of **7** suffered from low crystal quality, corrected this false assumption. Figures 3 and 4 show that both complexes are isostructural. Both contain tetrahedral zinc in the very common ZnN$_2$Hal$_2$ environment. Due to the small bite angle of the tridentate ligand the tetrahedral symmetry is distorted, resulting in a rather large Hal–Zn–Hal angle. The Zn–N and Zn–Hal distances of both complexes are in the known range for tetrahedral species (see above). The bonding details within the noncoordinated pyrazole units do not differ significantly from those within the coordinated ones. The structure determinations of **6** and **7** provided the proof that the tris(pyrazolyl)methane ligands are not reliably tridentate towards zinc. They share this weakness with the tris(aminomethyl)ethane[6] and the bis(pyrazolyl)(thienyl)methane[26] ligands.

Figure 2. The bis-ligand complex cation of **4**. Selected bond lengths [Å]: Zn−N1 2.182(2), Zn−N2 2.168(3), Zn−N3 2.148(2). − Bond angles [°]: N1−Zn−N2 84.1(1), N1−Zn−N3 83.6(1), N2−Zn−N3 84.4(1), N1−Zn−N2' 96.0(1), N1−Zn−N3' 96.4(1), N2−Zn−N3' 95.6(1)

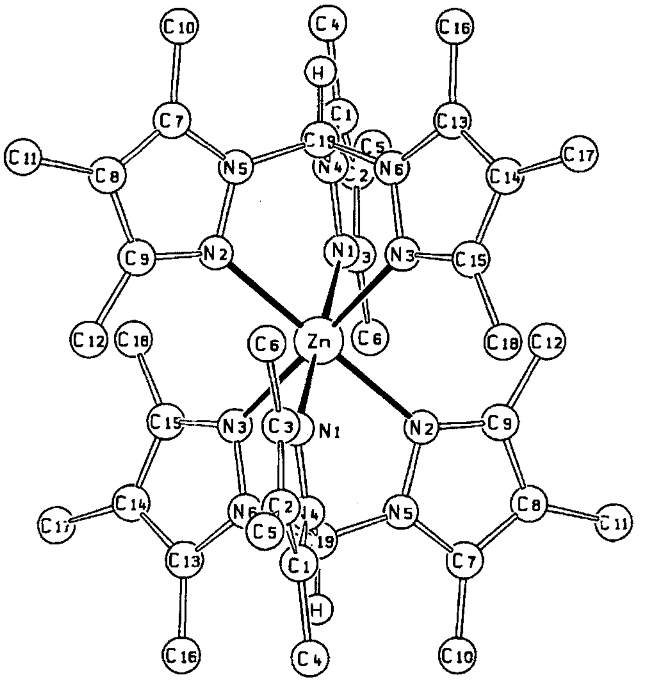


Figure 3. Molecular structure of **6**. Selected bond lengths [Å]: Zn−N11 2.038(2), Zn−N21 2.051(3), Zn−Cl1 2.223(1), Zn−Cl2 2.219(1). − Bond angles [°]: N11−Zn−N21 93.2(1), N11−Zn−Cl1 111.3(1), N11−Zn−Cl2 111.7(1), N21−Zn−Cl1 110.2(1), N21−Zn−Cl2 112.8(1), Cl1−Zn−Cl2 115.5(4)

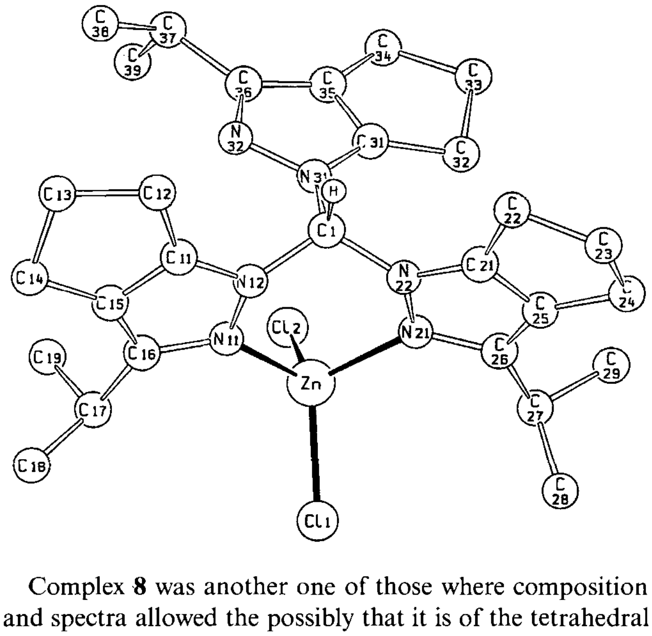
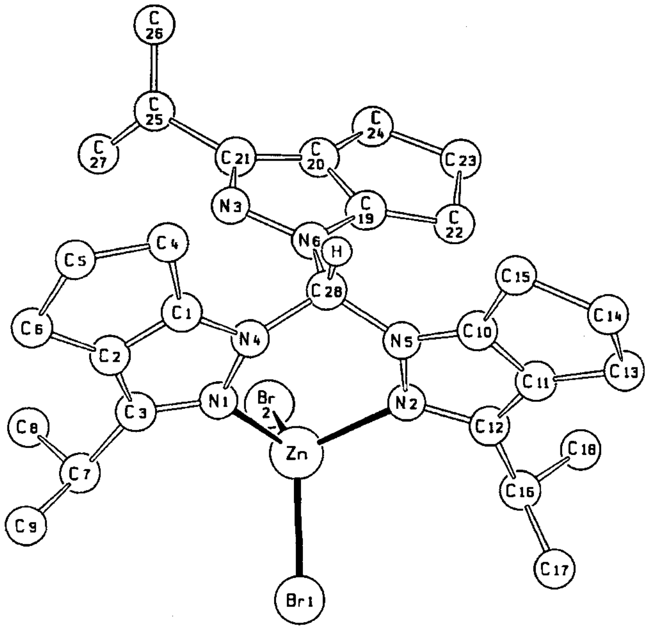


Figure 4. Molecular structure of **7**. Selected bond lengths [Å]: Zn−N1 2.02(2), Zn−N2 2.03(2), Zn−Br1 2.338(3), Zn−Br2 2.356(3). − Bond angles [°]: N1−Zn−N2 93.9(6), N1−Zn−Br1 110.4(4), N1−Zn−Br2 113.0(4), N2−Zn−Br1 108.9(4), N2−Zn−Br2 112.7(5), Br1−Zn−Br2 115.8(1)

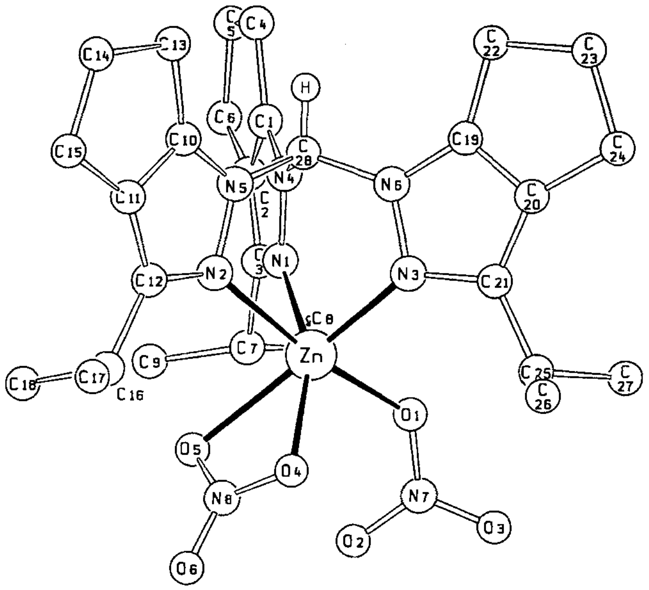


Complex **8** was another one of those where composition and spectra allowed the possibly that it is of the tetrahedral [L^4 · Zn−X]X type. Again the structure determination disproved this possibility in yet another way (Figure 5). The complex is octahedral with a tridentate L^4 and monodentate as well as bidentate nitrate ligands. This type of coordination does not occur with tris(pyrazolyl)borate zinc nitrates[27,28], but we observed it in [tris(pyridyl)phosphane]-zinc nitrate[8]. The latter complex anticipated the structural characteristics of **8**, i.e. the distinctly asymmetrical coordination of the bidentate nitrate ligand and its small bite angle of 59.1(2)°, the *trans* effect of the monodentate nitrate elongating the Zn−N2 bond, the untypically large N1−Zn−N3 angle [91.6(2)°] as compared to N1−Zn−N2 [83.6(2)°] and N2−Zn−N3 [82.7(2)], and the overall shortness of the four non-elongated Zn−O and Zn−N bonds. The comparison of the tetrahedral halide complexes **6** and **7** on one side and the octahedral oxo anion complex **8** on the other side substantiates the general trend in zinc chemistry relating softness with low and hardness with high coordination numbers.

Conclusion

Five new tris(pyrazolyl)methane ligands were obtained which, due to their encapsulating and tridentate nature, should prove useful for a stereocontrolled or biomimimetic metal complex chemistry. Their ligation behavior towards zinc parallels that of other uncharged tripods of the $A(B-C)_3$ type, i.e. they form 1:1 and 2:1 complexes, they use two or three of their donor functions, they go along with octahedral and tetrahedral coordination of zinc in a way that is not related to their bulkiness, and it is quite difficult to incorporate them in tetrahedral L^n · Zn−X com-

Figure 5. Structure of complex **8** with tridentate **L**^{4}. Selected bond lengths [Å]: Zn–N1 2.041(5), Zn–N2 2.329(5), Zn–N3 2.068(5), Zn–O1 2.088(5), Zn–O4 2.079(5), Zn–O5 2.228(9)



plexes. The main lesson to be learned from their zinc complex chemistry seems to be that their lack of a negative charge [which is present in the tris(pyrazolyl)borates] results in complex stabilities which are no longer high enough to favour tridentate coordination. While this may be less a problem with metals that form more stable complexes it introduces a rather high degree of unpredictability into their zinc chemistry.

This work was supported by the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft*. We are obliged to Prof. *W. Kaim*, Universität Stuttgart, for making complex **7** and its structure determination available to us.

Experimental

The general experimental techniques and spectroscopic methods were as described in ref.[29]. Metal salts were obtained commercially. The pyrazoles **HPz**^{1}–**HPz**^{7} were prepared from the corresponding β-diketones and hydrazine hydrate according to the procedures of Elguero and Jaquier[30], as practised various times by Trofimenko[31]. The phase-transfer catalyst (designated in the following as "catalyst") used for the tris(pyrazolyl)methane syntheses was an 80% solution of alkyl(C_8–C_{18})benzyldimethylammonium chlorides in benzene (Merck index 1066). All new compounds were characterized analytically (Table 3).

Tris(pyrazolyl)methane Ligands

General Procedure: The pyrazole and the catalyst were dissolved in benzene. A 33% NaOH solution in water was added to the resulting solution. Chloroform/benzene (1:1) was then added dropwise and slowly with vigorous stirring. After a further period of stirring 20 ml of a saturated NaCl solution in water was added. The two-phase reaction mixture was extracted with three portions of the extractand. The combined extracts were dried with Na_2SO_4, evaporated to dryness, and the residue was worked up.

Table 3. Analytical characterizations

	formula (mol. wt.)	elemental analyses (calcd./found) C	 H	 N	 Zn
L^3	$C_{25}H_{40}N_6$	70.71	9.49	19.79	
	(424.7)	70.60	9.39	19.06	
L^4	$C_{28}H_{40}N_6$	73.00	8.75	18.25	
	(460.7)	72.88	8.60	18.13	
L^5	$C_{31}H_{46}N_6$	74.06	9.22	16.72	
	(502.8)	73.89	9.18	16.53	
L^6	$C_{37}H_{34}N_6$	78.97	6.09	14.94	
	(562.7)	78.43	6.10	14.68	
L^7	$C_{46}H_{52}N_6$	80.19	7.61	12.20	
	(689.0)	79.90	7.38	12.05	
1	$C_{30}H_{48}Cl_2N_6O_8Zn$	47.60	6.39	11.10	8.64
	(757.1)	48.17	6.50	10.51	8.44
2	$C_{16}H_{28}Br_2N_4Zn$	38.31	5.63	11.17	13.04
	(501.6)	38.08	5.53	11.63	12.35
3	$C_{24}H_{24}N_6O_6Zn$	51.67	4.34	15.07	
	(557.9)	51.37	4.33	14.77	
4	$C_{38}H_{56}Cl_2N_{12}O_8Zn$	48.28	5.97	17.79	6.92
	(945.3)	47.87	5.84	17.60	6.88
5	$C_{16}H_{22}Br_2N_6Zn$	36.70	4.24	16.05	12.49
	(523.6)	37.02	4.20	16.07	12.50
6	$C_{28}H_{40}Cl_2N_6Zn\cdot CH_3CN$	56.48	6.79	15.37	
	(638.0)	56.35	6.83	15.17	
7	$C_{28}H_{40}Br_2N_6Zn$	49.03	5.88	12.26	9.53
	(685.9)	48.90	5.86	11.97	9.07
8	$C_{28}H_{40}N_8O_6Zn\cdot C_2H_5OH$	51.76	6.66	16.10	
	(696.2)	50.98	6.45	15.96	
9	$C_{28}H_{40}BrClN_6O_4Zn$	47.67	5.72	11.92	9.27
	(705.4)	47.27	5.64	11.78	9.60
10	$C_{28}H_{42}Cl_2N_6O_9Zn$	45.26	5.70	11.31	8.80
	(743.0)	43.31	5.22	10.76	8.82

L^1: From 0.96 g (10.0 mmol) of **HPz**^{1}, 0.1 ml of catalyst, 12 ml of benzene, 4.0 g of NaOH, and 4.0 ml of CHCl at 60 °C for 2 h. Extraction with 100 ml of ether. The raw product was dissolved in 50 ml of boiling hexane, the solution was filtered hot and left to stand at −30 °C to allow a black tar to deposit. The clear solution was decanted, evaporated to dryness and the residue sublimed at 140 °C/0.1 Torr to yield 243 mg (24%) of light yellow **L**^{1}[13], m.p. 149–152 °C. – IR (KBr, cm^{-1}): 1569 s (ring). – ^{1}H NMR ($CDCl_3$): δ = 1.94 (s, 9H, 5-Me), 2.11 (s, 9H, 3-Me), 5.80 (s, 3H, 4-H), 8.00 (s, 1H, methyne).

L^2: From 1.10 g (10.0 mmol) of **HPz**^{2}, 0.1 ml of catalyst, 12 ml of benzene, 4.0 g of NaOH, and 4.0 ml of $CHCl_3$ at 60 °C for 2 h. Workup as before and sublimation at 160 °C/0.1 Torr yielded 357 mg (31%) of colorless **L**^{2}[14], m.p. 180–182 °C. – IR (KBr, cm^{-1}): 1588 s (ring). – ^{1}H NMR ($CDCl_3$): δ = 1.88 (s, 9H, 4-Me), 1.93 (s, 9H, 5-Me), 2.13 (s, 9H, 3-Me), 8.00 (s, 1H, methyne).

L^3: From 1.38 g (10.0 mmol) of **HPz**^{3}, 0.1 ml of catalyst, 12 ml of benzene, 4.0 g of NaOH, and 4.0 ml of $CHCl_3$ at 60 °C for 2 h.

The raw product was dissolved in 20 ml of ether and subjected to column chromatography (3 × 30 cm, silica gel, eluent toluene/ethyl acetate/triethylamine, 50:45:5). The resulting solid was sublimed at 200°C/0.1 Torr to yield 100 mg (7%) of colorless $\mathbf{L}^3$, m.p. 54–56°C. – IR (KBr, cm^{-1}): 1555 s (ring). – ^1H NMR ($CDCl_3$): δ = 1.13 (s, 27H, *t*Bu), 1.91 (s, 9H, 5-Me), 5.81 (s, 3H, 4-H), 8.00 (s, 1H, methyne).

$\mathbf{L}^4$: From 1.50 g (10.0 mmol) of $\mathbf{HPz}^4$, 0.1 ml of catalyst, 12 ml of benzene, 4.0 g of NaOH, and 4.0 ml of $CHCl_3$ with ice cooling and subsequent warming up to room temp. for 2 h. Extraction with 100 ml of ether. The raw product was taken up in boiling pentane, the solution filtered while hot and left to stand at −30°C to allow a green tar to deposit. The solution was decanted, reduced in volume and cooled again. This procedure was repeated until no more tar deposited. The remaining solution was evaporated to dryness and the residue recrystallized from pentane to yield 380 mg (25%) of colorless $\mathbf{L}^4$, m.p. 108–110°C. – IR (KBr, cm^{-1}): 1558 s (ring). – ^1H NMR ($CDCl_3$): δ = 1.19 (d, J = 7.0 Hz, 18H, *i*Pr), 1.91 (t, J = 7.2 Hz, 6H, CH_2), 2.35 (tt, J = 7.0 Hz, CH_2), 2.55 (t, J = 6.8 Hz, 6H, CH_2), 2.90 (sept, J = 7.0 Hz, 3H, *i*Pr), 7.94 (s, 1H, methyne).

$\mathbf{L}^5$: From 1.64 g (10.0 mmol) of $\mathbf{HPz}^5$, 0.1 ml of catalyst, 12 ml of benzene, 4.0 g of NaOH, and 4.0 ml of $CHCl_3$ at room temp. for 2 h. Workup as for $\mathbf{L}^4$ and recrystallization form pentane yielded 0.76 g (45%) of colorless $\mathbf{L}^5$, m.p. 155–160°C. – IR (KBr, cm^{-1}): 1559 m (ring). – ^1H NMR ($CDCl_3$): δ = 1.25 (s, 27H, *t*Bu), 1.87 (t, J = 7.2 Hz, 6H, CH_2), 2.32 (tt, J = 7.0 Hz, 6H, CH_2), 2.58 (t, J = 6.8 Hz, 6H, CH_2), 7.92 (s, 1H, methyne).

$\mathbf{L}^6$: From 0.92 g (5.0 mmol) of $\mathbf{HPz}^6$, 0.2 ml of catalyst, 30 ml of benzene, 2.0 g of NaOH, and 2.0 ml of $CHCl_3$ at 50°C for 2 h. Extraction with 75 ml of benzene. The raw product was recrystallized three times from chloroform to yield 243 mg (26%) of colorless $\mathbf{L}^6$, m.p. 255°C (dec.). – IR (KBr, cm^{-1}): 1556 w (ring). – ^1H NMR ($CDCl_3$): δ = 2.31 (t, J = 7.0 Hz, 6H, CH_2), 2.52 (m, 6H, CH_2), 2.84 (t, J = 7.0 Hz, 6H, CH_2), 7.37 (m, 9H, Ar), 7.78 (m, 6H, Ar), 8.23 (s, 1H, methyne).

$\mathbf{L}^7$: From 2.26 g (10.0 mmol) of $\mathbf{HPz}^7$, 0.25 ml of catalyst, 30 ml of benzene, 4.0 g of NaOH, and 4.0 ml of $CHCl_3$ at 50°C for 2.5 h. Extraction with 60 ml of chloroform. The raw product was treated with 10 ml of methanol to remove impurities. The remaining solid was dried and recrystallized twice from cyclohexane/chloroform (5:1) to yield 620 mg (27%) of colourless $\mathbf{L}^7$, m.p. 240°C (dec.). – IR (KBr, cm^{-1}): 1552 w (ring). – ^1H NMR ($CDCl_3$): δ = 1.26 (d, J = 6.9 Hz, 18H, *i*Pr), 2.27 (t, J = 6.9 Hz, 6H, CH_2), 2.49 (m, 6H, CH_2), 2.81 (t, J = 6.9 Hz, CH_2), 2.92 (sept, J = 6.9 Hz, 3H, *i*Pr), 7.24 (d, J = 8.2 Hz, 6H, Ar), 7.69 (d, J = 8.2 Hz, 6H, Ar), 8.22 (s, 1H, methyne).

Complexes

1: A solution of 111 mg (0.29 mmol) of $Zn(ClO_4)_2 \cdot 6\,H_2O$ in 20 ml of methanol was added dropwise with stirring to a solution of 150 mg (0.29 mmol) of $\mathbf{L}^5$ in 20 ml of methanol. After 3 h of stirring the solvent was removed in vacuo. The residue was dissolved in a few ml of benzene, the solution heated to reflux for 30 min and filtered hot. After 3 d at room temp. 118 mg (52%) of **1** had precipitated as colorless crystals, m.p. 255–260°C. – IR (KBr, cm^{-1}): 3359 m, br, 3234 m, br (NH), 1583 m (ring), 1146 s, br, 1025 vs, 911 s (coord. ClO_4), 1093 vs, br (noncoord. ClO_4). – ^1H NMR ([D_6]acetone): δ = 1.38 (s, 27H, *t*Bu), 2.48 (m, 12H, CH_2), 2.78 (t, J = 6.9 Hz, 6H, CH_2), 4.52 (s, 3H, NH).

2: A mixture of 100 mg (0.19 mmol) of $\mathbf{L}^3$ and 44 mg (0.19 mmol) of anhydrous $ZnBr_2$ in 30 ml of methanol was stirred for 3 h. Removal of the solvent in vacuo left a residue which according to ^1H-NMR analysis contained a mixture of products with **2** as the main component. Repeated recrystallization yielded traces of analytically pure **2**. Using the same procedure, we obtained from 100 mg (0.72 mmol) of $\mathbf{HPz}^3$ and 81 mg (0.36 mmol) of $ZnBr_2$ 107 mg (58%) of **2** as colorless crystals, m.p. 84–86°C. – IR (KBr, cm^{-1}): 3135 m, br (NH), 1560 vs (ring). – ^1H NMR ($CDCl_3$): δ = 1.34 (s, 18H, *t*Bu), 2.22 (s, 6H, 5-Me), 6.01 (s, 2H, 4-H).

3: A solution of 47 mg (0.18 mmol) of $Zn(NO_3)_2 \cdot 4\,H_2O$ in 1 ml of methanol was added to a solution of 100 mg (0.18 mmol) of $\mathbf{L}^6$ in 40 ml of dichloromethane. After the solution had been stirred for 2 h it was filtered through a membrane filter. Slow evaporation of the solvent from the filtrate led to the precipitation of 25 mg (12%) of colorless **3**, m.p. 175–180°C (dec.). – IR (KBr, cm^{-1}): 3269 m, br (NH), 1592 w (ring), 1384 s, br, 1238 s, br (coord. NO_3). – ^1H NMR ($CDCl_3$): δ = 2.58 (m, 4H, CH_2), 2.85 (m, 8H, CH_2), 7.50 (m, 6H, Ar), 7.73 (m, 4H, Ar).

4: A solution of 100 mg (0.29 mmol) of $\mathbf{L}^2$ and 54 mg (0.14 mmol) of $Zn(ClO_4)_2 \cdot 6\,H_2O$ in 40 ml of methanol was stirred for 3 h. The solvent was removed in vacuo and the residue recrystallized from dichloromethane/methanol (1:1) to yield 108 mg (77%) of **4** as colorless crystals decomposing above 320°C. – IR (KBr, cm^{-1}): 1588 m (ring), 1094 vs, br (noncoord. ClO_4). – ^1H NMR (CD_3OD): δ = 1.46 (s, 18H, 4-Me), 1.85 (s, 18H, 5-Me), 2.56 (s, 18H, 3-Me), 8.17 (s, 2H, methyne).

5: A solution of 75 mg (0.33 mmol) of anhydrous $ZnBr_2$ in 20 ml of methanol was added dropwise to a stirred solution of 100 mg (0.33 mmol) of $\mathbf{L}^1$ in 20 ml of methanol. After the solution had been stirred for 3 h the solvent was removed in vacuo and the residue recrystallized from water to yield 82 mg (46%) of **5** as colorless crystals, m.p. 298–300°C. – IR (KBr, cm^{-1}): 1566 s (ring). – ^1H NMR (D_2O): δ = 1.65 (s, 9H, 5-Me), 2.69 (s, 9H, 3-Me), 6.19 (s, 3H, 4-H), 8.19 (s, 1H, methyne).

Complex **6** was obtained as a side product during reactions of ligand $\mathbf{L}^4$ with ruthenium salts using metallic zinc as a reductant[20]. – IR (KBr, cm^{-1}): 1576 s (ring). – ^1H NMR ($CDCl_3$): δ = 1.11 (d, J = 6.0 Hz, 18H, *i*Pr), 2.54 (m, J = 6.0 Hz, 18H, CH_2), 3.23 (sept, J = 7.0 Hz, 3H, *i*Pr), 7.50 (s, 1H, methyne).

7: A solution of 48 mg (0.21 mmol) of anhydrous $ZnBr_2$ in 20 ml of methanol was added dropwise to a stirred solution of 100 mg (0.21 mmol) of $\mathbf{L}^4$ in 20 ml of methanol. After 3 h of stirring the solvent was removed in vacuo and the residue recrystallized from dichloromethane/methanol (1:1). The resulting colorless crystals consisted of **7** · CH_2Cl_2 as evidenced by the crystal structure determination. Upon prolonged pumping they lost the solvent of crystallization, leaving behind 71 mg (46%) of **7**, m.p. 235–238°C. – IR (KBr, cm^{-1}): 1564 m (ring). – ^1H NMR ([D_6]DMSO): δ = 1.16 (d, J = 6.9 Hz, 18H, *i*Pr), 1.89 (t, J = 7.0 Hz, 6H, CH_2), 2.31 (m, 6H, CH_2), 2.50 (t, J = 7.0 Hz, 6H, CH_2), 2.82 (sept, J = 6.9 Hz, 3H, *i*Pr), 7.83 (s, 1H, methyne).

8: A solution of 100 mg (0.21 mmol) of $\mathbf{L}^4$ and 56 mg (0.21 mmol) of $Zn(NO_3)_2 \cdot 4\,H_2O$ in 40 ml of methanol was stirred for 3 h. The solvent was removed in vacuo. The residue was taken up in a minimum amount of ethanol and placed in a refrigerator. After 2 weeks 25 mg (18%) of **8** · C_2H_5O had precipitated as colorless crystals, m.p. 168–170°C. – IR (KBr, cm^{-1}): 1564 m (ring), 1486 vs, br, 1288 s, br (coord. NO_3). – ^1H NMR ($CDCl_3$): δ = 1.19 (d, 18H, J = 6.9 Hz, *i*Pr), 2.64 (m, 12H, CH_2), 2.89 (t, J = 7.0 Hz, 6H, CH_2), 3.04 (sept, J = 6.9 Hz, 3H, *i*Pr), 8.29 (s, 1H, methyne).

9: A solution of complex **7**, prepared as above from 48 mg (0.21 mmol) of $ZnBr_2$ under inert gas in 40 ml of methanol, was treated dropwise with a solution of 49 mg (0.21 mmol) of $AgClO_4 \cdot H_2O$ in 10 ml of methanol. A cloudy precipitate formed immediately. After the solution had been stirred for 1 h it was filtered through a membrane filter. The filtrate was evaporated to dryness and the

Table 4. Crystallographic details

	1	**4**	**6** · CH_3CN	**7** · CH_2Cl_2	**8** · EtOH
formula	$C_{30}H_{50}Cl_2N_6O_8Zn$	$C_{38}H_{56}Cl_2N_{12}O_8Zn$	$C_{30}H_{43}Cl_2N_7Zn$	$C_{29}H_{42}Br_2Cl_2N_6Zn$	$C_{30}H_{46}N_8O_7Zn$
mol. wt.	759.0	945.2	638.0	770.8	696.2
cryst. from	C_6H_6	CH_3OH/CH_2Cl_2	CH_3OH/CH_3CN	CH_3OH/CH_2Cl_2	C_2H_5OH
crystalsize [mm]	0.6 x 0.3 x 0.3	0.5 x 0.5 x 0.2	0.5 x 0.5 x 0.3	0.5 x 0.5 x 0.3	0.5 x 0.4 x 0.2
colour	colourless	colourless	colourless	colourless	colourless
space group	P-1	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Z	2	2	4	4	4
a [Å]	10.687(2)	10.900(2)	9.148(2)	9.330(2)	9.607(2)
b [Å]	12.852(2)	11.720(2)	15.145(3)	15.763(3)	22.173(4)
c [Å]	14.902(2)	18.456(3)	23.559(5)	23.753(5)	16.820(3)
α [°]	68.61(3)	90	90	90	90
β [°]	75.72(2)	99.74(4)	95.61(3)	97.39(3)	103.53(3)
γ [°]	78.22(3)	90	90	90	90
V [Å³]	1832.1(3)	2323.7(3)	3248.4(12)	3464.3(12)	3483.5(11)
$d_{calc.}$ [g/cm³]	1.38	1.35	1.26	1.46	1.24
d_{found}[g/cm³]	1.40	1.37	1.26	1.42	1.27
μ[mm⁻¹]Mo-K_α	0.87	0.70	0.95	3.20	0.75
2 θ-range [°]	4-50	4-54	3-54	4-46	4-46
hkl-range	0 ≤ h ≤ 13	0 ≤ h ≤ 13	-6 ≤ h ≤ 11	0 ≤ h ≤ 10	-11 ≤ h ≤ 11
	-15 ≤ k ≤ 15	-14 ≤ k ≤ 0	-2 ≤ k ≤ 19	0 ≤ k ≤ 17	-27 ≤ k ≤ 0
	-17 ≤ l ≤ 18	-23 ≤ l ≤ 23	-30 ≤ l ≤ 29	-26 ≤ l ≤ 26	-20 ≤ l ≤ 0
reflections measured	7581	5334	7528	5366	7297
reflections used [I>2σ(I)]	5030	3725	5673	2355	3105
variables	424	290	361	346	400
R (unweighted)	0.063	0.048	0.055	0.108	0.065
residual electron	+ 1.0	+ 0.4	+ 0.9	+ 1.6	+ 0.6
densities (e/Å³)	- 0.9	- 0.5	- 0.8	- 1.4	- 0.6

residue recrystallized from dichloromethane/methanol (1:1) to yield 62 mg (41%) of colorless **9**, m.p. 240–244 °C (dec.). Complex **9** decomposes slowly in methanol solution at room temp. – IR (KBr, cm^{-1}): 1558 m (ring), 1089 s, br (noncoord. ClO_4). – ^1H NMR ([D$_6$]acetone): δ = 1.25 (d, 18H, J = 7.0 Hz, *i*Pr), 2.70 (m, 12H, CH_2), 3.15 (t, J = 7.4 Hz, 6H, CH_2), 3.33 (sept, J = 7.0 Hz, *i*Pr), 8.87 (s, 1H, methyne).

10: A solution of complex **7** prepared as above from 48 mg (0.21 mmol) of $ZnBr_2$ was treated as above with a solution of 98 mg (0.43 mmol) of $AgClO_4 \cdot H_2O$. After the mixture had been stirred for 1 h and filtered through a membrane filter the solvent was removed in vacuo. The residue was washed with 1 ml of dichloromethane/methanol (1:1) and dried in vacuo to afford 141 mg (87%) of **10** as a colorless powder, m.p. 125–130 °C, which decomposed upon attempted recrystallization. – IR (KBr, cm^{-1}): 1562 m (ring), 1090 s, br (noncoord. ClO_4). – ^1H NMR ([D$_6$]acetone): δ = 1.15 (d, J = 6.9 Hz, 18H, *i*Pr), 2.60 (m, 12H, CH_2), 3.13 (t, J = 7.1 Hz, 6H, CH_2), 3.30 (sept, J = 6.9 Hz, 3H, *i*Pr), 5.80 (s, 2H, coord. H_2O), 8.24 (s, 1H, methyne).

Structure Determinations[32]: Table 4 lists all crystallographic details. The crystals were obtained during the analytical purifications. Intensity data were obtained by means of the ω/2Θ technique with a nonius CAD4 diffractometer. The structures were solved by direct methods and refined anisotropically without an absorption correction. Hydrogen atoms were included at fixed positions (C–H = 0.96 Å) with a common isotropic temperature factor. All calculations were done with the SHELX program system[33], drawings were produced using SCHAKAL[34].

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