On the Ligating Properties of Sulfonate and Perchlorate Anions Towards Zinc☆

Thomas Brandsch, Friedrich-Alexander Schell, Karl Weis, Michael Ruf, Bodo Müller, and Heinrich Vahrenkamp*

Institut für Anorganische und Analytische Chemie der Universität Freiburg,
Albertstraße 21, D-79104 Freiburg, Germany

Received September 4, 1996

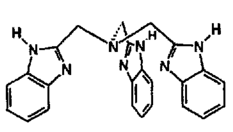
Keywords: Zinc / Sulfonate ligands / Perchlorates / Coordination modes

Attempts are reported to incorporate sulfonate and perchlorate anions as ligands in zinc complexes of tripodal ligands. Using tris(benzimidazolylmethyl)amine (BIMA) only the aqua complexes $[(BIMA)Zn-OH_2](RSO_3)(ClO_4)$ and $[(BIMA)Zn-OH_2](RSO_3)_2$ (R = CH_3, CF_3, *p*-tolyl) were accessible. Using substituted pyrazolylborates (Tp*), the same three sulfonate anions were found to be ligands in the complexes $Tp^*Zn-OSO_2R$. Spectroscopic evidence for perchlorate coordination in $Tp^*ZnClO_4 \cdot 2$ DMSO conflicts with crystallograpic evidence against it in $Tp^*ZnClO_4 \cdot$ pyridine. The crystal structures of $[(BIMA)Zn-OH_2](CH_3SO_3)_2$, $Tp^{Cum,Me}Zn-OSO_2CH_3$, $TP^{tBu,Me}Zn-OSO_2C_6H_4$-*p*-$CH_3$, and $[Tp^{Cum,Me}Zn \cdot NC_5H_5]ClO_4$ were determined.

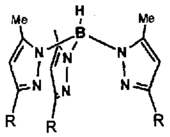
While the coordination chemistry of carbonates, carboxylates, nitrates or phosphates is well developed, the oxo anions of sulfur and of the halogens are typical representatives of the class of weakly coordinating anions[1–3]. This is inconvenient in terms of synthesis of their complexes, but it should be an advantage in terms of reactivity, because such complexes should be useful starting materials for other complexes of weakly coordinating ligands. Thus, it can be assumed that a sulfate or perchlorate ligand is less firmly bound to a metal center and hence a better leaving group than for instance a water molecule or a typical nitrogen ligand.

Modern coordination chemistry gives reason to search for such complexes of easily replaceable coordinating anions. This is so because attractive substrates of metal-complex or metalloenzyme-catalyzed reactions, e.g. CO_2, alcohols or aldehydes, are weakly coordinating ligands themselves and thus require the absence of better donors which would block "their" coordination sites. It is along these lines that we investigate the coordination chemistry of zinc with "bad" ligands.

This paper reports our attempts to find zinc complexes with coordinated sulfonate and perchlorate anions. It was planned to limit the coordination sphere to just one available coordination site. For this purpose the neutral tripodal ligand tris(benzimidazolylmethyl)amine (BIMA) and the two anionic tripodal tris(pyrazolyl)borate ligands $Tp^{tBu,Me}$ and $Tp^{Cum,Me}$ were applied. We had found previously that the BIMA[4,5] and Tp* ligands[6–8] support the coordination of monodentate oxygen ligands in easily accessible LZn–X complexes. Perchlorate complexes of zinc have already been structurally characterized by others[9,10] and ourselves[11]. The Cambridge Crystallographic Data Base contains quite a number of entries on zinc-coordinated sulfate ions[12], and the structures of four zinc monodentate sulfonate complexes (one of them[13] also containing uncoordinated sulfonate) have been described[13–16].



BIMA



R = t-Bu: $Tp^{tBu,Me}$
R = C_6H_4-p-i-C_3H_7: $Tp^{Cum,Me}$

BIMA Complexes

We had already obtained a (BIMA)zinc *p*-toluenesulfonate, the spectra of which seemed to indicate coordination of the sulfonate[4]. However, this compound did not yield crystals of X-ray quality. We therefore tried to vary the preparative conditions and the organic constituents of the sulfonates. As shown below, only the aqua complexes **1** and **2** containing uncoordinated sulfonates were obtained by this approach.

$[(BIMA)Zn-OH_2](RSO_3)(ClO_4)$	$[(BIMA)Zn-OH_2](RSO_3)_2$
1a: R = CH_3	**2a**: R = CH_3
1c: R = *p*-tolyl	**2b**: R = CF_3
	2c: R = *p*-tolyl

The starting point of the reactions was the perchlorate salt **3**[4] (see below) which could not be prepared water-free. Its treatment with the sulfonic acids CH_3SO_3H and *p*-$CH_3-C_6H_4SO_3H$ (a reaction which was adapted from similar reactions of Tp^*Zn-OH complexes[7,8]) resulted only in anion exchange and formation of **1a** and **b**. By using an excess of CH_3SO_3H compound **2a** was obtained in which the second perchlorate ion, but not the water molecule, had been replaced by methanesulfonate. The analogous complex **2b** resulted from zinc triflate and BIMA in methanol. Although care was taken to avoid the presence of water in this reaction, the traces of water present in the reagents or in the solvent ended up as ligands of the zinc ion, thereby demonstrating the stability of the BIMA · $Zn-OH_2$ cation.

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Finally, the reaction of **3** with tetraethylammonium tosylate, in analogy with the previously reported one[4], was hoped to yield an anhydrous complex. Its result, however, was only another aqua complex, **2c**.

One reason for our failure to obtain the desired sulfonate complexes was our lack of success in preparing a water-free perchlorate complex. Neither the treatment of $[Zn(DMSO)_6](ClO_4)_2$[17] nor of $[Zn(CH_3OH)_6]SiF_6$[18] with BIMA in presumably anhydrous solvents could avoid the incorporation of water ligands. Similarly, treatment of the reaction mixture of $[Zn(H_2O)_6](ClO_4)_2$ and BIMA or the resulting complex with triethyl orthoformate or 2,2-dimethoxypropane as dehydrating reagents could not remove the water completely. The only isolable perchlorate compound was the aqua complex **3** which we have described before[4].

$[(BIMA)Zn-OH_2](ClO_4)_2$
3

The main indicator for the presence of an aqua ligand in all complexes **1**–**3** is its OH band in the IR spectrum (Table 1). It is very broad, thereby indicating that the water molecule is not isolated but involved in hydrogen bonding. This may also explain why the ν(SO) and ν(ClO) bands of the anions vary noticeably among different complexes containing the same anions (e.g. **1a**, **1c**, **3**). The IR bands of the BIMA ligand are nearly superimposable for the free and ligated form. Only the strong ring vibration band at $\tilde{\nu}$ = 1439 cm^{-1} in free BIMA is shifted to 1453–1456 cm^{-1} in the complexes, thereby underlining the imidazole coordination.

Table 1. Characteristic IR bands of complexes **1**–**3** (in KBr; cm^{-1})

	ν(H_2O)	anion	ν(SO/ClO)
1a	3400	CH_3SO_3	1229,1163,1045
		ClO_4	1138,1119,1085
1c	3390	p-$CH_3C_6H_4SO_3$	1244,1152,1041
		ClO_4	1152,1120
2a	3380	CH_3SO_3	1230,1161,1044
2b	3350	CF_3SO_3	1249,1173,1029
2c	3390	p-$CH_3C_6H_4SO_3$	1246,1141,1046
3	3360	ClO_4	1145,1115,1086

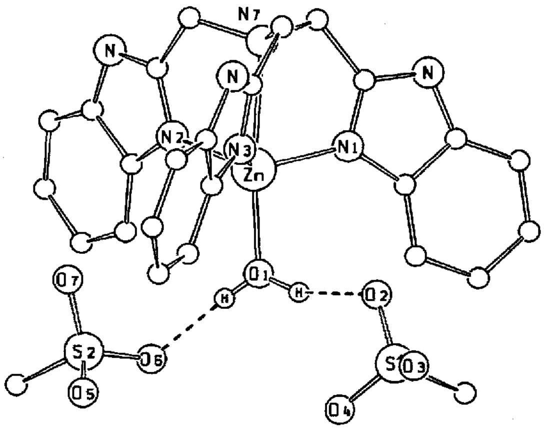
The aqua ligand also gives rise to a ^{1}H-NMR signal (Table 2) which in [D_6]DMSO does not exchange with the signal of the H_2O contained in the solvent and is of quite variable location. The latter indicates that the hydrogen bonding interactions persist in solution corresponding to cation-anion pairing. The sulfonate anions show their typical ^{1}H-NMR signals, as does the BIMA ligand[4,5]. Only one resonance of the BIMA ligand is of variable location (Table 2). It is due to the proton H_α of the aromatic ring closest to the zinc ion. It again reflects the change in the coordination environment brought about by the H_2O ligand's hydrogen-bonding interactions.

Table 2. Characteristic ^{1}H-NMR resonances of complexes **1**–**3** (in [D_6]DMSO; int. TMS)

	H_2O	H_α	anion
1a	3.64	8.32	2.79
1c	3.96	8.22	7.68(2H),7.22(2H),2.32(3H)
2a	3.46	8.41	2.63
2b	4.21	8.02	---
2c	3.42	8.10	7.55(2H),7.19(2H),2.30(3H)
3	3.68	8.00	---

A crystal-structure determination of **2a** (Figure 1) provided the basis for the constitutional assignment of all complexes **1**–**3**. The ligand environment of the zinc center is that of a distorted trigonal bipyramid with a very weak axial Zn–N interaction and a non-linear axial N–Zn–O arrangement, as previously observed for other (BIMA)zinc complexes with oxygen coligands[4,5]. Taking the N1, N2, N3, and O1 ligand atoms alone the coordination of the zinc ion may be described as tetrahedral to a good approximation. This also has precedence in zinc complexes of tetradentate tripod ligands, including the narrow spread of the four Zn–N and Zn–O distances[4,5,19].

Figure 1. Molecular structure of complex **2a**[a]



[a] Selected bond lengths [Å] and angles [°]: Zn–O1 2.011(3), Zn–N1 2.013(4), Zn–N2 2.017(4), Zn–N3 2.027(4), Zn–N7 2.463(4); O1–Zn–N1 99.6(2), O1–Zn–N2 110.5(2), O1–Zn–N3 102.2(2), O1–Zn–N7 172.9(2).

The two methanesulfonate anions are linked to the water ligand by hydrogen bonds (O1···O6 2.61 Å, O1···O2 2.83 Å). They also form hydrogen bonds via their oxygen atoms O2, O4, and O7 to the imidazole NH function of neighboring complexes. The S–O distances (uncoordinated 1.40–1.43 Å) are in the normal range, those involved in hydrogen bonding (S1–O2 1.44 Å, S2–O6 1.47 Å) are slightly elongated. Figure 1 was chosen such as to visualize that the cation-anion combination of complex **2a** is nearly a molecular entity.

Pyrazolylborate Complexes

The (pyrazolylborate) zinc unit had been shown to accommodate monodentate coligands whose HSAB properties range from very soft to very hard[6–8,20], and we had found that reaction of the hydroxide complexes Tp*Zn−OH with acids HX is a convenient way for the formation of complexes Tp*Zn−X[7,8,21,22]. The chances of obtaining (pyrazolylborate)zinc sulfonate complexes were therefore good, and one triflate, mesylate, and tosylate were actually prepared. When $Tp^{tBu,Me}Zn-OH$ or $Tp^{Cum,Me}Zn-OH$ were treated with equimolar amounts of the acids CH_3SO_3H, CF_3SO_3H, and p-$CH_3C_6H_4SO_3H$ the spectra indicated in all cases that the corresponding sulfonate complexes were formed. However, partial hydrolytic destruction of the pyrazolylborates was also observed leading to reaction mixtures which were difficult to separate. Only from $Tp^{tBu,Me}Zn-OH$ and toluenesulfonic acid could the pure complex **4c** be isolated. The alternative reaction of the pyrazolylborates with the zinc sulfonates was successful for $KTp^{Cum,Me}$ in combination with $Zn(CH_3SO_3)_2$ and $Zn(CF_3SO_3)_2$, respectively. The resulting complexes were **5a** and **b**.

$Tp^{tBu,Me}Zn-OSO_2R$
4c: R = p-$CH_3C_6H_4$

$Tp^{Cum,Me}Zn-OSO_2R$
5a: R = CH_3
5b: R = CF_3

The spectroscopic evidence for the formation of complexes **4** and **5** is listed in Tables 3 and 4. While the ^1H-NMR signals and IR bands of the pyrazolylborate ligands show little variation in comparison to those of other Tp* Zn complexes[6,8], the bands attributable to the sulfonate anions are characteristic. While the NMR data of the coordinated and uncoordinated sulfonates cannot be compared due to the change of solvents, the IR bands show typical shifts in going from complexes **1** and **2** to complexes **4** and **5**. Therefore, they are a strong indicator of a possible sulfonate ligation.

Table 3. Characteristic IR bands of complexes **4** and **5** (in KBr; cm^{-1})

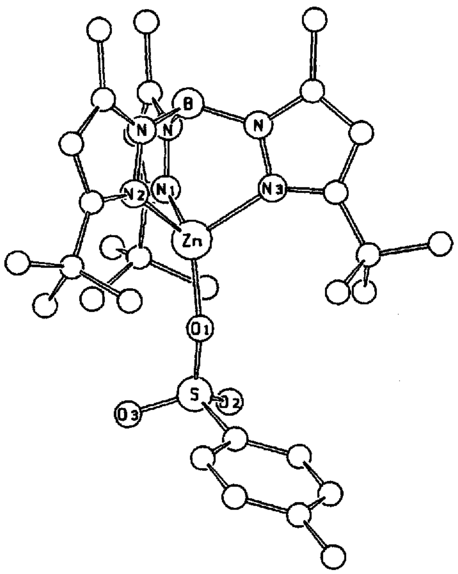
	ν(BH)	ν(SO)
4c	2552	1295, 1185, 1163
5a	2552	1291, 1186
5b	2545	1269, 1179, 1144

Table 4. Characteristic NMR resonances of complexes **4** and **5** ($CDCl_3$, int. TMS)

	δ(sulfonate)
4c	7.92(2H), 7.24(2H), 2.38(3H)
5a	2.10(3H)
5b	−77.0(^{19}F NMR, rel. $CFCl_3$)

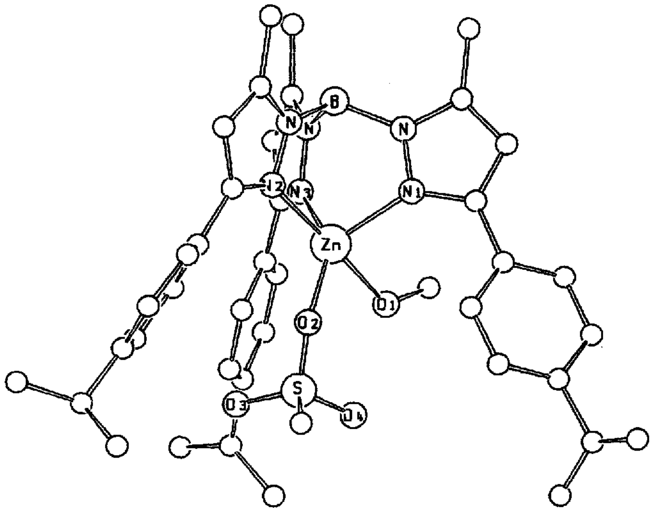
Complexes **4c** and **5a** could be subjected to crystal-structure determinations, cf. Figures 2 and 3. They prove the monodentate nature of the sulfonate ligands. As was already obvious from the synthesis of **4c** from the Zn−OH complex, the sulfonates are better ligands in this context than the water constituents. The structure of **5a** shows in addition that the sulfonates can also coexist with protic ligands (here methanol) in the ligand sphere of the zinc ion.

Figure 2. Molecular structure of **4c**[a]



[a] Selected bond lengths [Å] and angles [°]: Zn−O1 1.889(3), Zn−N1 2.030(3), Zn−N2 2.025(3), Zn−N3 2.036(3), O1−S 1.486(4), S−O2 1.420(4), S−O3 1.432(4); O1−Zn−N1 128.9(1), O1−Zn−N2 118.5(1), O1−Zn−N3 116.0(1), Zn−O1−S 152.9(2).

Figure 3. Molecular structure of **5a**[a]



[a] Selected bond lengths [Å] and angles [°]: Zn−O1 2.17(1), Zn−O2 1.96(1), Zn−N1 2.05(1), Zn−N2 2.15(1), Zn−N3 2.02(2), O2−S 1.49(1), S−O3 1.45(1), S−O4 1.47(1) Å; O1−Zn−N2 177.2(5), O2−Zn−N3 139.4(6), O1−Zn−O2 84.2(4), Zn−O2−S 140.8(8).

In complex **4c** the coordination about the zinc ion is quite symmetrical (see Zn−N distances and O−Zn−N angles). The Zn−N distances and the short Zn−O distance are of the usual length[6,8,20,21], and the pyrazolylborate ligand shows no peculiarities. In complex **5a** the situation is quite different. Zinc is five-coordinate, and its coordination geometry is that of a severely distorted trigonal bipyramid with O1 and N2 on the axial positions. While it was formerly believed that sterically demanding pyrazolylborate ligands enforce tetrahedral coordination about the zinc ion, it has now become obvious that they do allow fivefold coordination with geometries ranging from square-pyramidal to trigonal-bipyramidal[21−23]. Due to the increase in coordination number all zinc-ligand bond lengths in **5a** are longer than those in **4c**, especially those for the axial ligands. Another feature of **5a** which is worth mentioning is the hydrogen-bonding network which links the zinc-coordinated methanol molecule with the sulfonate ligand which in turn is linked via O3 and O4 to two further methanol molecules one of which is linked to yet another one. This observation is significant in terms of enzyme modelling by Tp*Zn complexes as there is a very polar assembly of molecules inside the hydrophobic pocket built by the three cumenyl substituents.

The sulfonate ligands in complexes **4c** and **5a** contain sulfur atoms which are tetrahedral to a reasonable degree. Their coordinating oxygen atoms have S−O bonds which are typically longer (average 0.04 Å) than the others. Otherwise they compare favourably with those in **2a** and in other zinc sulfonate complexes[13−16]. Both observed Zn−O−S angles are considerably larger than those in the other zinc sulfonate complexes (124−139°), which may result from the fact that the Zn−O−S unit has only a limited degree of freedom inside the pyrazolylborate ligand's pocket.

Assuming that the perchlorate ligand is the best leaving group from zinc complexes we made many attempts to obtain a $Tp^*Zn{-}OClO_3$ complex. So far they have not led to an undoubtable result. The treatment of both Tp*Zn−OH complexes with perchloric acid caused hydrolytic destruction of the Tp* ligands. Using water-free zinc perchlorates, e.g. $[Zn(EtOH)_6](ClO_4)_2$ or $[Zn(MeOH)_6](ClO_4)_2$ which are accessible from $[Zn(H_2O)_6](ClO_4)_2$ by dehydration with orthoesters or 2,2-dimethoxypropane[24] was not successful either. Both their alcoholic solutions and the isolated salts seemed to contain enough water to allow the formation of the preferred hydroxo complexes Tp*Zn−OH. In each case the impure solids obtained by removing the solvent showed several perchlorate IR bands thereby indicating the presence of zinc-coordinated perchlorate, but the desired complexes resisted isolation.

Only the perchlorates $[Zn(DMSO)_6](ClO_4)_2$[17] and $[Zn(py)_4](ClO_4)_2$[25] containing the better donors dimethyl sulfoxide and pyridine, and therefore being less hygroscopic, allowed the formation of water-free (pyrazolylborate)zinc perchlorates. The former with $KTp^{Cum,Me}$ resulted in complex **6**, the latter in complex **7**. Both complexes showed a strong tendency to hydrolyse to $Tp^{Cum,Me}Zn{-}OH$ and therefore had to be handled in the absence of moisture.

$Tp^{Cum,Me}ZnClO_4 \cdot 2\ DMSO$
6

$Tp^{Cum,Me}ZnClO_4 \cdot$ pyridine
7

The ^1H-NMR data for the $Tp^{Cum,Me}$ ligand of **6** differ little from those of other $Tp^{Cum,Me}Zn{-}OX$ complexes and therefore are of little diagnostic value. The DMSO ^1H-NMR signal and the IR data, however, can be interpreted in terms of coordinated perchlorate and non-coordinated DMSO for **6**. There is only one DMSO signal at $\delta = 2.31$ in $CDCl_3$. Assuming monodentate coordination of one DMSO ligand at tetrahedral zinc and slow ligand exchange one would expect separate NMR signals for the coordinated and uncoordinated DMSO molecules. Of the three ν(ClO) bands at $\tilde{\nu} = 1181$, 1095 and 1065 cm^{-1} the highest one is typically shifted to higher wavenumbers in comparison to those of the noncoordinating perchlorates in **1a**, **1c**, and **3**. The same effect is observed when comparing the ν(SO) bands of the coordinated sulfonates in **4** and **5** with those of the uncoordinated ones in **1**−**3**. In addition, the ν(SO) band of DMSO ($\tilde{\nu} = 1056$ cm^{-1} in the free state), which is observed at $\tilde{\nu} = 1021$ cm^{-1} for $[Zn(DMSO)_6](ClO_4)_2$, does not show up as a strong band in the region $\tilde{\nu} = 1050{-}1000$ cm^{-1} in the IR spectrum of **6** and may be hidden under the perchlorate band at $\tilde{\nu} = 1065$ cm^{-1}. Since suitable crystals of **6** could not be obtained this constitutional assignment is somewhat doubtful.

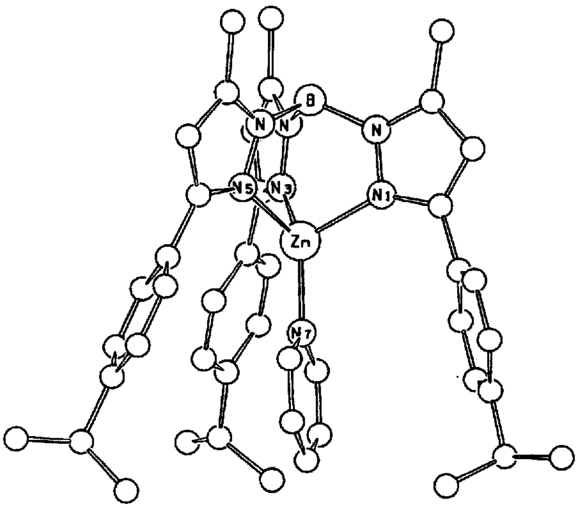
The perchlorate IR bands observed for **7** ($\tilde{\nu} = 1171$, 1093, 1067 cm^{-1}), just like for **6**, point to perchlorate coordination. This time, however, common sense (pyridine being too good a donor) and the ^1H-NMR data (see Experimental Section) speak against it. The aromatic resonances of the cumenyl groups are shifted upfield by 0.3−0.6 ppm compared to those of $Tp^{Cum,Me}Zn{-}OH$, and likewise the pyridine resonances are shifted upfield by 0.5−1.5 ppm compared to those of free pyridine. In both cases the mutual ring-current effect is responsible for the shifts which we have observed in similar cases before[8,26]. These data indicate a location of the pyridine ring between the cumenyl substituents and hence its coordination to the zinc ion.

Proof for this was obtained by a structure determination of **7**, cf. Figure 4. Compound **7** is a quite symmetrical complex with a trigonally distorted tetrahedral ZnN_4 coordination. The perchlorate ion is not disordered and not associated with any of the complex cation's constituents.

While the Zn−N distances of the Tp ligand are in the normal range, the Zn−N(pyridine) distance must be considered as long compared to the usual Zn−O distances in Tp*Zn−OX complexes[6,8,20] or to the corresponding Zn−N distance of 1.93 Å in $[Tp^{Cum,Me}Zn \cdot$ 2-methylimidazole]ClO_4[26]. On the other hand simple tetrahedral zinc complexes, e.g. $[Zn(imidazole)_4](ClO_4)_2$[27], also show Zn−N distances of 1.98−2.00 Å. The disk-like shape of the pyridine ligand which does not allow a good fit between the three cumenyl substituents is the reason for the distortions from the ideal trigonal symmetry around the zinc ion.

This work has shown once again the superior quality of the substituted pyrazolylborate ligands for the fixation of labile coligands by encapsulation. While neither the sulfonates nor perchlorate could be attached to the (BIMA)zinc unit it was no problem to bind the sulfonates to the Tp*Zn unit. We are optimistic that proof for a perchlorate coordi-

Figure 4. Structure of the complex cation of **7**[a]



[a] Selected bond lengths [Å] and angles [°]: Zn−N7 1.967(3), Zn−N1 2.020(3), Zn−N3 1.992(3), Zn−N5 2.027(3); N7−Zn−N1 115.9(1), N7−Zn−N3 130.2(1), N7−Zn−N5 120.4(1), N1−Zn−N3 96.8(1), N1−Zn−N5 93.3(1), N3−Zn−N5 92.1(1).

nation to the latter can also be found. The challenge to make zinc complexes with very weakly bound ligands as precursors for highly functional or catalytic zinc compounds persists.

This work was supported by the *Deutsche Forschungsgemeinschaft* and by the *Fonds der Chemischen Industrie*. We thank Dr. *W. Deck* for help with the NMR and X-ray work.

Experimental Section

General experimental methods and measuring techniques: see ref.[28]. The starting complexes **3**[4], $Tp^{tBu,Me}Zn{-}OH$[6], $Tp^{Cum,Me}Zn{-}OH$[8] and their tripodal ligands were prepared as described before. The zinc salts, sulfonic acids and their salts, and the organic reagents were obtained commercially. All solvents were carefully dried.

1a: 100 mg (0.15 mmol) of **3** was dissolved with warming in 10 ml of ethanol and treated with 15 mg (0.15 mmol) of CH_3SO_3H. After heating to reflux for 2 h, the mixture was filtered hot and the filtrate allowed to cool down slowly. 72 mg (70%) of **1a** were precipitated as colorless crystals, m.p. 305 °C (dec.), which were filtered off and dried in vacuo. − $C_{25}H_{26}ClN_7O_8SZn$ (685.5): calcd. C 43.81, H 3.82, N 14.31, Zn 9.54; found C 43.78, H 3.57, N 13.95, Zn 9.37.

1c: Like **1a** from 100 mg (0.15 mmol) of **3** and 30 mg (0.15 mmol) of p-$CH_3C_6H_4SO_3H \cdot H_2O$. Yield 86 mg (75%) of colorless **1c**, m.p. 325 °C (dec.). − $C_{31}H_{30}ClN_7O_8SZn$ (761.6): calcd. C 48.89, H 3.97, N 12.88, Zn 8.59; found C 49.37, H 3.81, N 12.95, Zn 8.28.

2a: Like **1a** from 100 mg (0.15 mmol) of **3** and 30 mg (0.31 mmol) of CH_3SO_3H. Allowing the mother liquor to stand for 2 weeks led to the precipitation of 56 mg (55%) of **2a** as colorless

Table 5. Crystallographic data of the complexes **2a**, **4c**, **5a** and **7**

	2a	**4c**	**5a**	**7**
formula	$C_{26}H_{29}N_7O_7S_2Zn$	$C_{31}H_{47}BN_6O_3SZn \times 0.5\ CH_3CN$	$C_{41}H_{53}BN_6O_4SZn \times 2.5\ CH_3OH$	$C_{44}H_{51}BClN_7O_4Zn$
mol. mass	681.05	680.51	882.24	853.55
cryst. size [mm]	0.5×0.3×0.2	0.5×0.4×0.3	0.4×0.2×0.2	0.6×0.5×0.4
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group	*P*1bar	$P2_1/n$	$P2_1/n$	*P*1bar
Z	2	4	4	2
a [Å]	10.213(8)	10.638(1)	15.796(3)	13.341(1)
b [Å]	13.295(11)	21.598(2)	14.539(3)	13.639(1)
c [Å]	14.105(9)	15.955(1)	21.485(4)	14.835(1)
α [°]	109.94(6)	90	90	116.07(1)
β [°]	109.55(6)	91.595(4)	107.30(3)	90.03(1)
γ [°]	99.54(7)	90	90	111.93(1)
V [nm^3]	1.609(2)	3.6644(5)	4.7110(16)	2.2049(3)
$d_{calcd.}$ [gcm^{-3}]	1.41	1.23	1.24	1.29
$d_{obsd.}$ [gcm^{-3}]	1.40	1.24	1.20	1.26
μ(Mo-K_α) [mm^{-1}]	0.95	0.77	0.62	0.67
Θ range [°]	2.8-26.5	2.3-26.0	3.7-22.0	3.0-26.0
hkl range	$-12 \le h \le 12$	$-13 \le h \le 13$	$-16 \le h \le 7$	$-16 \le h \le 16$
	$0 \le k \le 16$	$-26 \le k \le 0$	$-15 \le k \le 6$	$-16 \le k \le 15$
	$-17 \le l \le 16$	$0 \le l \le 19$	$-21 \le l \le 22$	$0 \le l \le 18$
refl. measd.	6886	7435	6041	9003
indep. refl.	6592	7175	5754	8650
obs. refl. [$I > 2\sigma(I)$]	4861	4708	1940	5834
parameters	388	415	424	523
R (obs. refl.)	0.057	0.046	0.095	0.052
wR_2 (all refl.)	0.202	0.159	0.299	0.157
res. el. dens. [e/Å^3]	+1.1 −0.5	+0.4 −0.5	+0.5 −0.4	+0.7 −0.3

crystals, m.p. 325°C (dec.). – $C_{26}H_{29}N_7O_7S_2Zn$ (681.1): calcd. C 45.85, H 4.29, N 14.40, Zn 9.60; found C 44.41, H 3.67, N 14.27, Zn 9.86.

2b: 265 mg (0.65 mmol) of BIMA were dissolved in 5 ml of methanol with warming and combined with a solution of 236 mg (0.65 mmol) of $Zn(CF_3SO_3)_2$ in 5 ml of methanol. After 2 h of stirring, the volume was reduced to 2 ml in vacuo and 2 ml of diethyl ether was added with stirring. 253 mg (49%) of colorless **2b**, m.p. 285°C (dec.) was slowly precipitated, which was filtered off, washed with diethyl ether and dried in vacuo. – $C_{26}H_{23}F_6N_7O_7S_2Zn$ (789.1): calcd. C 39.58, H 2.94, N 12.43, Zn 8.29; found C 38.34, H 3.08, N 11.46, Zn 8.53.

2c: 100 mg (0.15 mmol) of **3** was dissolved with warming in 10 ml of ethanol and treated with a solution of 90 mg (0.30 mmol) of $(Et_4N)(p\text{-}CH_3C_6H_4SO_3)$ in 2 ml of ethanol. After heating to reflux for 2 h, the volume was reduced in vacuo to 5 ml. Within a few days, 95 mg (76%) of **2c**, colorless crystals, m.p. 340°C (dec.) was precipitated, which were filtered off and dried in vacuo. – $C_{38}H_{37}N_7O_7S_2Zn$ (833.3): calcd. C 54.77, H 4.48, N 11.77, Zn 7.85; found C 53.96, H 4.42, N 11.59, Zn 8.06.

4c: 200 mg (0.395 mmol) of $Tp^{tBu,Me}Zn{-}OH$ and 75.1 mg (0.395 mmol) of $p\text{-}CH_3C_6H_4SO_3H \cdot H_2O$ in 20 ml of dichloromethane were stirred for 16 h. Then the solvent was removed in vacuo. Recrystallization of the residue from acetonitrile yielded 240 mg (91%) of colorless crystalline **4c** · 1/2 CH_3CN, m.p. 244°C. – $C_{31}H_{47}BN_6O_3SZn \cdot 1/2\ CH_3CN$ (680.5): calcd. C 56.48, H 7.18, N 13.38; found C 56.09, H 7.10, N 13.14.

5a: 51 mg (0.20 mmol) of $Zn(CH_3SO_3)_2$ in 5 ml of methanol was treated with a solution of 97 mg (0.20 mmol) of $KTp^{Cum,Me}$ in 3 ml of dichloromethane and the mixture was stirred for 1 h. The volume was reduced to 2 ml in vacuo. Warming of the solution to dissolve the precipitate and slow cooling to 4°C yielded 83 mg (54%) of **5a** as colorless crystals, m.p. 136°C, which were filtered off and dried in vacuo. – $C_{41}H_{53}BN_6O_4SZn$ (802.2): calcd. C 61.39, H 6.66, N 10.48, Zn 8.15; found C 60.82, H 6.19, N 10.64, Zn 8.43.

5b: 200 mg (0.31 mmol) of $KTp^{Cum,Me}$ in 20 ml of dichloromethane was treated with stirring with a solution of 112 mg (0.31 mmol) of $Zn(CF_3SO_3)_2$ in 20 ml of methanol. A precipitate was formed immediately which was filtered off after 1 h of stirring, washed with little methanol and dried in vacuo, leaving 183 mg (72%) of **5b** as colorless powder, m.p. 232°C. – $C_{40}H_{46}BF_3N_6O_3SZn$ (824.1): calcd. C 58.30, H 5.63, N 10.20; found C 58.16, H 5.78, N 10.45.

6: 131 mg (0.18 mmol) of $[Zn(DMSO)_6](ClO_4)_2$[17] in 5 ml of methanol was treated with a solution of 87 mg (0.18 mmol) of $KTp^{Cum,Me}$ in 3 ml of dichloromethane. After stirring for 15 h, the solution was filtered and the filtrate reduced to 2 ml in vacuo. The precipitate formed was redissolved by warming. Upon standing at 4°C, 104 mg (62%) of colorless **6**, m.p. 173°C, was precipitated which was filtered off and dried in vacuo. – $C_{43}H_{58}BClN_6O_6S_2Zn$ (930.8): calcd. C 55.49, H 6.28, N 9.03, Zn 7.03; found C 54.87, H 6.10, N 8.87, Zn 7.18.

7: Solutions of 600 mg (1.30 mmol) of $KTp^{Cum,Me}$ and 670 mg (1.03 mmol) of $[Zn(pyridine)_4](ClO_4)_2$[25] in 25 ml of pyridine each were combined and stirred for 1 d. The solution was filtered and the filtrate evaporated to dryness in vacuo. The residue was picked up in 10 ml of toluene and 5 ml of dichloromethane. Removal of the dichloromethane in vacuo resulted in the formation of a precipitate. This was filtered off, washed with pentanes, and dried in vacuo, leaving 490 mg (55%) of colorless **7**, m.p. 195°C (dec.). – ^1H NMR ($CDCl_3$): δ = 7.97 (t, J = 7.7 Hz, 1H, Py-4), 7.16 (d, J = 8.0 Hz, 6H, Ph-2 and Ph-6), 7.07 (d, J = 4.9 Hz, 2H, Py-2 and Py-6), 7.02 (d, J = 8.0 Hz, 6H, Ph-3 and Ph-5), 6.88 (dd, J = 7.7 and 4.9 Hz, 2H, Py-3 and Py-5), 6.24 (s, 3H, Pz-H), 2.83 (sept, J = 6.9 Hz, 3H, CH-*i*Pr), 2.61 (s, 9H, Pz-CH_3), 1.16 (d, J = 6.9 Hz, 18H, CH_3-*i*Pr). – $C_{44}H_{51}BClN_7O_4Zn \cdot 1/2\ CH_2Cl_2$ (853.6 + 42.5): calcd. C 59.65, H 5.65, N 10.94, Zn 7.30; found C 60.50, H 5.83, N 11.14, Zn 7.32.

Structure Determinations[29]: Crystals of **2a** and **4c** were taken as obtained from the preparations, those of **5a** were produced by slow evaporation from methanol, those of **7** by slow evaporation from dichloromethane/petroleum ether (b.p. 30–50°C). The data sets were obtained with a Nonius CAD4 diffractometer by the $\omega/2\Theta$ technique using graphite-filtered Mo-K_α radiation. An absorption correction based on azimutal scans was applied to **4c**. The structures were solved with direct methods and refined anisotropically. H atoms were included with C–H = N–H = 0.96 Å and isotropic temperature factors 1.2 times those of their attached atoms (1.5 times in methyl groups). The structures refined well without disorder in the perchlorate or sulfonate ions. The outermost of the loosely bound methanol molecules in **5a** is not well-defined due to half occupancy (possibly due to loss from the crystal during data collection). The computer programs by Sheldrick[30] and Keller[31] were used. Table 5 lists the crystallographic data.

☆ Dedicated to Professor *Günter Schmid* on the occasion of his 60th birthday.

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