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A zinc–aldimine complex

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Dedicated to Professor Dirk Walther on the occasion of his 60th birthday.

Abstract

Dimethylaminobenzaldimine-zinc-bis(pentafluorothiophenolate) was obtained from the reaction of dimethylaminobenzaldehyde with ammonia-contaminated zinc-bis(pentafluorothiophenolate) and characterized by a structure determination. Zinc effects the catalytic formation and stabilization of the aldimine by complexation. \bigcirc 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Aldehyde imines, the simplest of all Schiff bases, are not stable at room temperature, undergoing condensation and polymerization reactions [1]. Blocking the unshared electron pair on nitrogen should lower their lability, typically by coordination to a transition metal. In accord with this, it was observed many years ago by Pfeiffer, in the developing phase of the salen ligands, that chelating aldehyde ligands react with ammonia to form aldimine complexes. The most typical of these are derived from substituted salicylic aldehydes [2], but the reaction was also observed for coordinated pyrrolyl aldehyde [3]. Subsequently, nickel and copper complexes of 3-alkoxysalicyl-aldimines were structurally characterized and used for the formation of dinuclear complexes [4-8], and one copper complex of pyrrolyl-2-aldimine [9] was subjected to crystal structure determinations. In the field of zinc chemistry the electronic spectra of a few salicylaldimine complexes have been reported [10,11], and copper and nickel salicylaldimine complexes were used as 'ligands' for zinc salts [12]. These few reports justify the statement that very little use has been made of the complex-stabilized aldimines, neither in organic chemistry nor in coordination chemistry.

We came across this class of complexes during our studies of zinc aldehyde complexes in the context of the modelling of the zinc enzyme alcohol dehydrogenase [13]. We had modelled the coordination environment of the zinc ion in this enzyme by the 2-dimethylaminobenzalde-hyde-zinc-thiolate complex 1. Complex 2 is the aldimine analogue of 1. This paper describes the synthesis and molecular structure of 2. 2 is the first fully characterized zinc complex of an aldimine, and it has for the first time been possible to compare the structures of an aldehyde and the corresponding aldimine complexes.



2. Results and discussion

2.1. Preparation

The aldimine complex 2 was found accidentally when preparing complex 1 from zinc-bis(pentafluorothiophenolate) and dimethylaminobenzaldehyde [13]. Since water is a better ligand for zinc than aldehydes, completely

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Fig. 1. Molecular structures of 2. (a): ring-parallel conformers in 2a, 2b and 2c(1). (b): ring-separated conformer in 2c(2).

water-free conditions had to be ensured. This was done for the zinc thiolate by preparing it from zinc-bis-(bistrimethylsilylamide) and pentafluorothiophenol [14], overlooking originally that the product obtained is contaminated with ammonia and silylamide components [15] resulting from partial thiolysis of $Zn[N(SiMe_3)_2]_2$. Consequently the combination of the aldehyde and the zinc thiolate produced a mixture of **1** and **2**.

After the successful isolation of pure 2 it could be verified that careful treatment of pure 1 [13] with water-free ammonia yields 2, i.e. the conversion of the aldehyde to the imine can take place in the ligand sphere of zinc. This, however, is not a favourable process for the preparation of 2 due to the efforts involved in obtaining pure 1 and separating the product mixture resulting from 1 and NH₃. Instead we found an easy way to separate 1 and 2 by using tetrahydrofuran as a solvent. The latter is a better ligand for zinc than dimethylaminobenzaldehyde and allowed for the crystallization of uncontaminated 2 from THF/CH₂Cl₂ solutions.

Complex 2 was characterized by its IR absorptions (in KBr) at 3208 cm⁻¹ for the NH stretch and at 1627 cm⁻¹ for the C=N unit, both of medium intensity. In the ¹H NMR spectrum (for details see Section 3) the aldimine function shows up in the form of two characteristic doublets at 11.19 and 8.87 ppm for the NH and CH units, respectively. In the ¹³C NMR spectrum the aldimine carbon resonance is observed at 176.7 ppm. A heteronuclear COSY experiment with indirect ¹⁵N detection confirmed the presence of the imine nitrogen.

2.2. Structure

Our original doubts about the identities of 1 and 2 led to many attempts at separation and crystallization. As

a result three different polymorphs of $2(2\mathbf{a}-\mathbf{c})$ were found and subjected to structure determinations. In addition the orthorhombic crystals of $2\mathbf{c}$ contain two formula units per asymmetric unit, bringing the number of independent molecular structures to four. Thus the structure determination of 2 offered a unique opportunity to compare crystallographic and 'real' standard deviations of bond lengths and angles.

The molecular shapes of **2** in crystals of **2a**, **2b** and one independent unit of **2c** are practically identical, as displayed in Fig. 1(a). The other independent unit in **2c** is another conformer, differing by a rotation about the Zn–S axes, as shown in Fig. 1(b). While in the latter the two C_6F_5 rings of the complex do not interact with each other (but with phenyl rings of neighbouring molecules), in the three other conformers they are parallel, showing a stacking interaction with ring-to-ring distances of approximately 3.3 Å.

The bond lengths in the four independent molecular structures (Table 1) show a remarkable uniformity, with only those for **2c**, having the crystals of lowest quality, differing more than three standard deviations from the average values. This demonstrates that packing forces have little influence on the bond distances for this complex. In contrast, there is a larger spread of the 'softer' bond angles, specifically of the N–Zn–S angles and the Zn–N–C angles. Yet even here the total variation of the values is small. This applies also to the two different conformers in **2c**. In particular the Zn–S, S–C, and C=N bonds as well as the N–Zn–N and NH–C–C angles are practically constant throughout the series.

Typical molecular features are the large S–Zn–S and small N–Zn–N angles, as observed in many other com-

Table 1 Bond lengths (Å) and angles (°) in the crystals of 2

	2a	2b	2c (1)	2c (2)
Zn–N(NH)	2.023(1)	2.007(4)	2.073(10)	2.021(9)
$Zn-N(NMe_2)$	2.149(2)	2.142(4)	2.118(10)	2.166(9)
Zn-S1	2.286(1)	2.302(1)	2.283(3)	2.283(3)
Zn–S2	2.281(1)	2.283(1)	2.280(3)	2.275(3)
C=N(NH)	1.275(2)	1.273(6)	1.254(15)	1.273(14)
$C-N(NMe_2)$	1.452(2)	1.454(5)	1.498(15)	1.487(13)
S1–C	1.762(1)	1.757(4)	1.763(12)	1.778(11)
S2–C	1.756(1)	1.754(4)	1.750(12)	1.751(12)
S1–Zn–S2	120.9(1)	115.8(1)	125.1(1)	122.9(1)
N–Zn–N	87.3(1)	89.8(1)	88.8(4)	88.4(4)
S1–Zn–N(NH)	114.9(1)	121.5(1)	113.5(3)	112.4(2)
S2–Zn–N(NH)	111.8(1)	117.0(1)	113.0(3)	112.2(3)
$S1-Zn-N(NMe_2)$	109.9(1)	107.6(1)	103.0(3)	108.8(3)
$S2-Zn-N(NMe_2)$	106.4(1)	102.7(1)	105.3(2)	106.2(3)
Zn–NH–C	121.1(1)	124.2(3)	120.4(9)	123.6(8)
Zn–NMe ₂ –C	107.6(1)	111.7(3)	104.6(7)	109.2(6)
NH-C-C	124.8(1)	125.8(4)	124.3(12)	125.6(11)

plexes with ZnN_2S_2 coordination [16]¹. The Zn–S bond lengths are normal for tetrahedral zinc with terminal thiolate [16]. The Zn–N(imine) and Zn–N(amine) bond lengths differ significantly due to the different radii of sp^2 and sp^3 nitrogen. The Zn–N(imine) distances are quite short, even for tetrahedral zinc and also when compared to Zn–N distances for heterocyclic nitrogen ligands or Schiff-base complexes. This indicates a strong coordination ability of the aldimine function. In contrast the Zn–N(amine) bonds are rather long. This corresponds to our experience that tertiary amines are weak ligands for zinc and bind well only in a favourable chelating situation, an example with a similar bonding situation being a complex with a chelating pyrrolidine donor [17].

The chelating aldimine ligand offers no unusual bonding features. Bond lengths and angles in the C-CH=NH unit are comparable to those in the three other structurally characterized aldimine complexes [4–9]. Coordination geometries and chelating situations cannot be compared as all three reported complexes are square planar and derived from different aldimines.

2.3. Comparison of the aldehyde and aldimine complexes

The aldimine complex 2 is more stable than the aldehyde complex 1. This is not only obvious from its spontaneous formation but also from its behaviour in solution and in the solid state. While 1 is decomposed by traces of moisture (e.g. the atmosphere), and even

weak ligands like THF or acetone replace the aldehyde ligand, 2 can be transferred as a solid into the open atmosphere and was isolated from THF solution. Exposure to water in solution, however, also leads to the decomposition of 2.

The molecular shapes of 1 and 2 (the three ring-parallel conformers, Fig. 1(a) are practically superimposable. The orientation of the SC₆F₅ groups and the folding of the six-membered chelate rings are nearly identical. The only noteworthy differences lie in the Zn-N and Zn-O bond distances. The Zn-N(NH) bond in **2** is about 0.08 Å shorter than the Zn–O(aldehyde) bond in 1, in contrast to the increase in atomic radii from O to N. This bond strengthening is compensated by a bond weakening for the Zn-N(NMe₂) bond which in 2 is about 0.045 Å longer than that in 1. Taking the large variability of Zn-N bond lengths (even when maintaining tetrahedral coordination) the observed changes from 1 to 2 are not dramatic. They are in accord with the increased chemical stability of 2, but cannot provide the sole explanation for it. We would therefore invoke the ZnN₂S₂ coordination, which is highly favored in the classical and biological coordination chemistry of zinc, as the main reason of stability. Thereby the inherent lability of the unsubstituted imine function is overcome, firstly by coordination to a metal and secondly by the advantageous coordination mode.

3. Experimental

The general experimental methods and measuring techniques were as in Ref. [13,18]. 2-Dimethylaminobenzaldehyde [19] and $Zn[N(SiMe_3)_2]_2$ [20] were prepared as described. $Zn(SC_6F_5)_2$ [21] was synthesized by Bochmann's method [14] from $Zn[N(SiMe_3)_2]_2$ and C_6F_5SH .

3.1. Preparation of 2

A total of 5.08 g (10.96 mmol) of $Zn(SC_6F_5)_2$ were dissolved in 25 ml of diethyl ether and a few drops of THF. 1.64 g (10.99 mmol) of 2-dimethylaminobenzaldehyde in 5 ml of diethyl ether was added dropwise with stirring. Upon slow addition of 200 ml of petroleum ether (b.p. 60-70°C) an orange-yellow precipitate formed consisting of an approximately 1:1 mixture of 1 and 2. After filtration the precipitate was dissolved in a minimum amount of THF/CH2Cl2 and the solution layered with petroleum ether. Within 1 day yellow crystals of 2 were formed which were filtered off, washed with petroleum ether and dried in vacuo. 2.35 g (35%) of 2, m.p. 130°C (dec.), were obtained. ¹H NMR (acetone-d₆): 3.02 [s, 6H, CH₃(NMe₂)], 7.42 [m, 1H, H5], 7.63 [m, 1H, H3], 7.68 [m, 2H, H4, H6], 8.87 [d, ${}^{3}J = 14.7$ Hz, 1H, CH(Imine)], 11.19 [d, ${}^{3}J = 14.7$ Hz,

¹ Comparisons were made with structures deposited in the Cambridge Crystallographic Data Centre.

Table 2	
Crystallographic	details

	2a	2b	2c
Formula	$C_{21}H_{12}F_{10}N_2S_2Zn$	$C_{21}H_{12}F_{10}N_2S_2Zn$	$C_{21}H_{12}F_{10}N_2S_2Zn$
Molecular weight	611.82	611.82	611.82
Crystallization from	THF/CH ₂ Cl ₂	THF/hexane	THF/CH ₂ Cl ₂ /hexane
Crystal size (mm)	$0.5 \times 0.5 \times 0.4$	$1.0 \times 0.8 \times 0.7$	$0.5 \times 0.1 \times 0.07$
Space group	$P\overline{1}$	$P\overline{1}$	Pbca
Ζ	2	2	16
a (Å)	8.770(3)	7.492(3)	14.238(2)
b (Å)	12.043(3)	12.039(3)	12.650(2)
c (Å)	12.189(3)	13.180(5)	49.857(9)
α (°)	111.24(2)	83.78(3)	90
β (°)	105.48(3)	74.50(3)	90
γ (°)	97.14(3)	79.94(2)	90
$V(Å^3)$	1120.8(5)	1125.6(7)	8980(3)
$D_{\rm calc} \ ({\rm g} \ {\rm cm}^{-3})$	1.81	1.81	1.81
μ (Mo K α) (mm ⁻¹)	1.38	1.37	1.38
θ Range (°)	2.5-28.0	3.0-26.5	2.5-24.5
hkl Ranges	$-11 \le h \le 0$	$-9 \le h \le 0$	$-16 \le h \le 0$
	$-15 \leq k \leq 15$	$-15 \le k \le 14$	$0 \leq k \leq 14$
	$-15 \le l \le 16$	$-16 \le l \le 16$	$-58 \leq l \leq 0$
No. reflections measured	5740	5062	7590
No. independent reflections	5392	4698	7587
No. reflections observed $(I > 2\sigma)$	4987	4361	4051
Parameters ref.	325	325	649
R (observed reflections)	$R_1 = 0.023, \ wR_2 = 0.061$	$R_1 = 0.058, \ wR_2 = 0.210$	$R_1 = 0.077, \ wR_2 = 0.170$
R (all reflections)	$R_1 = 0.027, wR_2 = 0.064$	$R_1 = 0.062, wR_2 = 0.218$	$R_1 = 0.206, \ wR_2 = 0.221$
Residual electron density (e $Å^{-3}$)	+0.4	+0.9	+3.0
	-0.5	-1.1	-1.6

1H, NH(Imine)]. ¹³C NMR (acetone-d₆): 47.4 [CH₃(NMe₂)], 121.2, 126.5, 127.4 [s, C1, C3, C5], 135.9, 137.2 [s, C4, C6], 135.5, 140.3, 145.1, 146.3, 150.5 [m, C₆F₅], 176.7 [CN(Imine)]. ¹⁹F NMR (acetone-d₆): -133.0 [d, ³*J* = 23.0 Hz, 4F, F2,6], -164.2 [t, ³*J* = 20.7 Hz, 2F, F4], -165.5 [t, ³*J* = 20.7 Hz, 4F, F3,5]. *Anal.* Calc. for C₂₁H₁₂F₁₀N₂S₂Zn (611.9): C, 41.07; H, 1.97; N, 4.22; Zn, 10.74. Found: C, 41.23; H, 1.98; N, 4.58; Zn, 10.69%.

3.2. Structure determinations

Diffraction data were taken by the $\omega/2\theta$ technique on a Nonius CAD4 diffractometer using graphitefiltered Mo K α radiation. They were treated without an absorption correction. The structures were solved with direct methods and refined anisotropically with the SHELX program suite [22]. Hydrogen atoms were included with fixed distances and isotropic temperature factors 1.2 times those of their attached atoms. Parameters were refined against F^2 . In the case of **2c** the low quality of the crystals yielded a somewhat unsatisfactory data set resulting in a high *R* value and large standard deviations. The *R* values are defined as $R_1 = \Sigma |F_o| - |F_c| / \Sigma F_o$ and $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] /$ $\Sigma[w(F_o^2)^2]$ ^{1/2}. Drawings were produced with SCHAKAL [23]. Table 2 lists the crystallographic data.

4. Supplementary material

The crystallographic data of the structures described in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 134723–134725. Copies of these data are available free of charge from the following address: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: teched@ chemcrys.cam.ac.uk).

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