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Zinc complexes of cyclohexane triamine ligands

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Abstract

The synthesis and characterization of zinc complexes of the *cis*-cyclohexane triamine derived ligands $C_6H_9(NH_2)_3$ (L^1), $C_6H_9(NHMe)_3$ (L^2) and $C_6H_9(N{=}CHPh)_3$ (L^3) are described. L^1 forms 1:1 complexes with $ZnCl_2$, $ZnBr_2$, ZnI_2 and $Zn(OAc)_2$, and 2:1 complexes with $Zn(ClO_4)_2$ and $Zn(CF_3SO_3)_2$. For L^2, no 2:1 complexes with zinc salts could be obtained, but 1:1 complexes with $ZnCl_2$ and $Zn(NO_3)_2$ were obtained. L^3 was hydrolyzed in the presence of zinc salts. Physical properties and spectra indicate that the complexes of $ZnHal_2$ and $Zn(NO_3)_2$ contain tetrahedral LZnX cations and free X anions, while $L^1Zn(OAc)_2\cdot H_2O$ seems to consist of octahedral molecular units containing monodentate acetate ligands. According to NMR, the 2:1 complexes $(L^1)_2Zn(CF_3SO_3)_2$ and $(L^1)_2Zn(ClO_4)_2$ are octahedrally coordinated while $(L^1H)_2Zn(ClO_4)_4$ contains tetrahedral zinc with only bidentate L^1 ligands. A crystal structure determination has proved the octahedral geometry of $(L^1)_2Zn(CF_3SO_3)_2$. NMR studies have shown that there is no or little ligand exchange of the complexes in solution.

Introduction

In the active center of zinc containing enzymes, the zinc ion is mostly attached in a tetrahedral fashion to three amino acid side chains while a water molecule or a OH group occupies the fourth coordination site. This basic L_3ZnX arrangement has been found in several protein crystal structure determinations [1, 2], and various model studies have applied it [3–5]. Recent examples include mimicking phosphatase activity with ([12]ane N_3)Zn-OH [6] and the intensive discussion on the mechanism of carbonic anhydrase activity [7].

Our contributions to this field have so far evolved around the zinc coordination chemistry of tris(aminomethyl)methane and tris(pyrazolyl)borate derived ligands [8, 9]. In particular, the latter ligands have allowed structural and functional models of the enzyme carbonic anhydrase to be built [10, 11]. In this paper we wish to report on the isolation and characterization of zinc complexes of ligands derived from *cis*-cyclohexane triamine. This ligand which offers three amine donors in a stereochemically favourable orientation was expected to allow the preparation of further reactive L_3ZnX species.

cis-Cyclohexane triamine zinc complexes have been investigated before. Stabilities were determined titrimetrically by Schwarzenbach and Brauner [12] and thermochemically by Paoletti *et al.* [13]. A bis-ligand zinc nitrate was isolated by Wentworth [14] and a bis-ligand zinc chloride by Flückiger [15]. We wanted to increase the number of isolated and characterized complexes, and we wanted to focus on the 1:1 stoichiometry in order to obtain the desired tetrahedral and monofunctional L_3ZnX species.

Experimental

Materials and procedures

The general experimental techniques and physical measurements were as described before [16]. The ligands *cis*-cyclohexane triamine, $C_6H_9(NH_2)_3$, L^1 [17], *cis*-cyclohexane tris(methylamine), $C_6H_9(NHCH_3)_3$, L^2 [18], and *cis*-cyclohexane tris(benzylidene imine), $C_6H_9(N{=}CHC_6H_5)_3$, L^3 [18] were prepared according to the literature methods.

Synthesis of the complexes

1:1 Complexes

$L^1\cdot ZnCl_2$ (1a). To a solution of 122 mg (0.90 mmol) $ZnCl_2$ in 20 ml of ether/methanol (2:1) was added dropwise under stirring a solution of 116 mg (0.90 mmol) L^1 in 20 ml ether/methanol (2:1). A white precipitate formed immediately which was filtered off and dried in vacuum. The precipitate consisted of analytically pure **1a**, yield 229 mg(96%), m.p. 270 °C (dec.). IR (KBr): ν(NH)3257vs, 3204vs, 3126s; ν (CH) 2952w, 2905m cm^{-1}. NMR (CD_3OD): 1.84 d, b, $J^2=15.2$ Hz, 3H, CH_2; 2.03 d, b, $J^2=15.2$ Hz, 3H, CH_2; 3.52 s, b, 3H, CH.

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Anal. Calc. for $C_6H_{15}Cl_2N_3Zn$ (M_r 265.5): C, 27.14; H, 5.69; N, 15.83. Found: C, 27.55; H, 5.72; N, 15.80%.

$L^1\cdot ZnBr_2$ (1b). To a solution of 242 mg (1.08 mmol) $ZnBr_2$ in 20 ml ethanol was added dropwise under stirring a solution of 139 mg (1.08 mmol) L^1 in 20 ml ethanol. The white precipitate was filtered off, washed with 5 ml ethanol and dried in vacuum yielding 281 mg (74%) of analytically pure **1d**, m.p. 320 °C (dec.). IR (KBr): ν(NH) 3259s, 3204s, 3126s; ν(CH) 2927m, 2852w, cm^{-1}. NMR (DMSO-d_6): 1.70 d, b, $J^2=15.1$ Hz, 3H, CH_2; 2.02 d, b, $J^2=15.1$ Hz, 3H, CH_2; 3.31 s, b, 6H, NH_2; 3.44 s, b, 3H, CH.

Anal. Calc. for $C_6H_{15}Br_2N_3Zn$ (M_r 354.4): C, 20.33; H, 4.27; N, 11.86. Found: C, 20.29; H, 4.08, N, 11.43%.

$L^1\cdot ZnI_2$ (1c). As for **1b** from 270 mg (0.85 mmol) ZnI_2 and 110 mg (0.85 mmol) L^1. The precipitate was recrystallized from ethanol/methanol (2:1) yielding 305 mg (80%) colourless crystals of **1c**, m.p. 255 °C (dec.). IR (KBr): ν(NH) 3252vs, 3206vs, 3126vs; ν(CH) 2946m, 2904s, 2852m, cm^{-1}. NMR (CD_3OD): 1.87 d, b, $J^2=15.2$ Hz, 3H, CH_2; 2.04 d, b, $J^2=15.2$ Hz, 3H, CH_2; 3.54 s, b, 3H, CH.

Anal. Calc. for $C_6H_{15}I_2N_3Zn$ (M_r 448.0): C, 16.07; H, 3.37; N, 8.37. Found: C, 15.66; H, 3.37; N, 8.87%.

$L^1\cdot Zn(CH_3COO)_2\cdot H_2O$ (1d). To a solution of 197 mg (0.90 mmol) $Zn(CH_3COO)_2\cdot 2H_2O$ in 10 ml ethanol was added dropwise under stirring a solution of 115 mg (0.89 mmol) L^1 in 10 ml ethanol. After stirring for 30 min the solvent was removed in vacuum. The resulting oily residue which solidified after a few days was recrystallized from ethanol/ether/pentane (1:2:5) yielding 252 mg (85%) colourless crystals of **1d**, m.p. 200 °C. IR (KBr): ν(OH) 3430–3350s, 3300s; ν(NH) 3261vs, 3162s; ν(CH) 2962w, 2928m, 2903m, 2882m; ν(CO) 1576vs, 1426sh, 1411s cm^{-1}; NMR (CD_3OD): 1.88 d, b, $J^2=15.4$ Hz, 3H, CH_2; 2.09 d, b, $J^2=15.4$ Hz, 3H, CH_2; 1.92s, 6H, CH_3; 3.54 s, b, 3H, CH.

Anal. Calc. for $C_{10}H_{21}N_3O_4Zn\cdot H_2O$ (M_r 330.7): C, 36.32; H, 7.01; N, 12.71. Found: C, 36.69; H, 6.44; N, 12.71%.

$L^2\cdot ZnCl_2$ (2a) To a solution of 66 mg (0.48 mmol) $ZnCl_2$ in 15 ml ethanol was added dropwise under stirring a solution of 84 mg (0.49 mmol) L^2 in 15 ml ethanol. After reducing the volume to 10 ml in vacuum a white precipitate was formed. This was filtered off and dried in vacuum yielding 84 mg (55%) of **2a**, m.p. 238 °C (dec.). IR (KBr): ν(NH) 3211sh, 3106vs; ν(CH) 2956s, 2921s, 2881s, 2821w cm^{-1}. NMR (CD_3OD): 1.94 d, b, $J^2=14.8$ Hz, 3H, CH_2; 2.36 d, b, $J^2=14.8$ Hz, 3H, CH_2; 2.57s, 9H, CH_3; 3.16s, b, 3H, CH.

Anal. Calc. for $C_9H_{21}Cl_2N_3Zn$(M_r 307.6): C, 35.14; H, 6.88; N, 13.66. Found: C, 35.62; H, 7.14; N, 13.56%.

$L^2\cdot Zn(NO_3)_2$ (2b). To a solution of 64 mg (0.29 mmol) $Zn(NO_3)_2\cdot 6H_2O$ in 10 ml ethanol was slowly added dropwise and under stirring a solution of 74 mg (0.58 mmol) L^2 in 2 ml ethanol. The white precipitate was filtered off, dried in vacuum and recrystallized from methanol yielding 64 mg (61%) of **2b**, m.p. 233 °C (dec.). IR (KBr): ν(NH) 3205m, 3121s; ν(CH) 2946sh, 2916m, 2825w; ν(NO) 1435sh, 1384vs, 1323w cm^{-1}. NMR (DMSO-d_6): 1.63 d, b, $J^2=15.0$ Hz, 3H, CH_2; 2.27 d, $J^3=6.0$ Hz, 9H, CH_3; 2.34 d, b, $J^2=15.0$ Hz, 3H, CH_2; 2.82 m, b, 3H, CH; 4.01 q, $J^3=6.0$ Hz, 3H, NH.

Anal. Calc. for $C_9H_{21}N_5O_6Zn$ (M_r 360.7): C, 29.97; H, 5.87; N, 19.42. Found: C, 29.94; H, 5.90; N, 19.15%.

2:1 Complexes

$L^1{}_2Zn(CF_3SO_3)_2$ (3a). To a solution of 137 mg (0.38 mmol) $Zn(CF_3SO_3)_2$ in 40 ml methanol was slowly added dropwise and under stirring a solution of 95 mg (0.74 mmol) L^1 in 20 ml methanol. The white precipitate was filtered off. Slow evaporation of the remaining solution led to a further batch of crystalline material. The combined yield of analytically pure **3a** (m.p. 250 °C (dec.)) was 179 mg (79%). IR (KBr): ν(NH) 3317vs, 3273vs, 3180m; ν(CH) 2927m, 2888m; ν(CF) 1268s; ν(SO) 1162s cm^{-1}. NMR (DMSO-d_6): 1.62 d, b, $J^2=15.4$ Hz, 6H, CH_2: 1.77 d, b, $J^2=15.4$ Hz, 6H, CH_2; 3.01 s, 12H, NH_2; 3.36 s, b, 6H, CH.

Anal. Calc. for $C_{14}H_{30}F_6N_6O_6S_2Zn$ (M_r 622.1): C, 27.04; H, 4.86; N, 13.51. Found: C, 27.15; H, 4.75; N, 13.38%.

$L^1{}_2Zn(ClO_4)_2$ (3b) Solutions of $Zn(ClO_4)_2\cdot 6H_2O$ (112 mg, 0.30 mmol) and L^1 (78 mg, 0.60 mmol), each in 10 ml methanol, were allowed to diffuse into one another through a C4 glass frit. After two weeks a crust of product had formed which was isolated and dried in vacuum yielding 61 mg (39%) analytically pure crystalline colourless **3b**, m.p. 255 °C (dec.). IR (KBr): ν(NH) 3270s, 3216s, 3134m; ν(CH) 2926m, 2876m; ν(ClO) 1175m, 1142vs, 1112vs, 1088vs cm^{-1}. NMR (DMSO-d_6): 1.60–1.94 m, 12H, CH_2; 3.01 s, b 6H, CH; 3.34 s, b, 12H, NH_2.

Anal. Calc. for $C_{12}H_{30}Cl_2N_6O_8Zn$ (M_r 522.7): C, 27.57; H, 5.79; N, 16.08. Found: C, 27.50; H, 5.68; N, 15.81%.

$L^1{}_2Zn(ClO_4)_2\cdot 2HClO_4$ (3c). Solutions of 158 mg (0.42 mmol) $Zn(ClO_4)_2\cdot 6H_2O$ and 55 mg (0.42 mmol) L^1, each in 10 ml water/methanol (10:1), were combined. The solution was filtered to remove a cloudy precipitate and left standing in an open beaker for evaporation. The last 5 ml of solvent were decanted off the crystalline

precipitate which was dried in vacuum yielding 61 mg (40%) of **3c**, m.p. 300 °C (dec.). IR (KBr): $\nu(NH_2)$ 3279sh, 3258s, 3205s, 3127s; $\nu(NH_3)$ 3038m, 2998sh, 2954s; $\nu(CH)$ 2925s, 2906s, 2857sh; $\nu(ClO_4)$ 1175m, 1146vs, 1111vs, 1088vs cm^{-1}. NMR (DMSO-d$_6$): 1.16–2.15 m, b, 18H, CH_2+CH; 3.01s, 8H, NH_2; 7.59 s, b, 6H, NH_3^+.

Anal. Calc. for $C_{12}H_{32}Cl_4N_6O_{16}Zn$ (M_r 723.6): C, 19.92; H, 4.46; N, 11.62; Zn, 9.04. Found: C, 20.00; H, 4.50; N, 11.75; Zn, 8.60%.

Reactions of L^3 with zinc salts

Combining alcoholic solutions of $ZnCl_2$, $ZnBr_2$, $Zn(SCN)_2$, $Zn(ClO_4)_2$ or $Zn(BF_4)_2$ with L^3 did not lead to the precipitation of complexes as for L^1 and L^2. NMR spectra of the solutions showed initially the presence of the seemingly uncoordinated ligand which decomposed upon standing for a day or during removal of the solvent in vacuum. The brownish oily residues remaining after removal of the solvent contained mixtures of decomposition products. In the case of the $Zn(BF_4)_2 \cdot 6H_2O$ reaction a chloroform extract of the oily residue contained benzaldehyde which was NMR spectroscopically almost pure and the amount of which corresponded to one third of the molar amount of the starting material L^3.

Structure determination

Crystals of **3a** (formula $C_{14}H_{30}F_6N_6O_6S_2Zn$, mol. wt. 622.1) were obtained by evaporation of a methanol solution, and a colourless prism of size 0.5×0.5×0.9 mm was chosen for the measurement. Crystals belong to the rhombohedral system, space group $R3$ with hexagonal axes $a=19.234(3)$, $c=23.582(5)$ Å, $V=7556(2)$ Å^3, $Z=12$, $D_{calc}=1.64$ g cm^{-3}, $\mu=12.4$ cm^{-1}. All crystallographic data were obtained with Mo Kα radiation with a Nonius CAD4 diffractometer. Of the 5935 reflections obtained with the ω–2θ technique in the range $\pm h \pm k + l$ for $2\theta = 2$–$43°$, 1984 were independent and all used for the calculations without an absorption correction. The SHELX program system [19] was used to solve the structure with Patterson methods and for the full matrix least-squares refinement. Anisotropic temperature factors were applied for the zinc and nitrogen atoms. Hydrogen atoms were included with a C–H bond length of 0.96 pm and a common isotropic temperature factor. The refinement for 236 variables converged to an unweighted R value of 0.058 and a *GOF* of 7.63. The largest peaks in the final difference map corresponded to +0.7 and −0.6 e/Å^3. Atomic parameters are given in Table 1, the structure drawing was produced with the SCHAKAL program [20]. See also 'Supplementary material'.

TABLE 1. Atomic parameters for **3a** (atomic coordinates ×10^4, equivalent isotropic temperature factors pm^2×10^{-1})

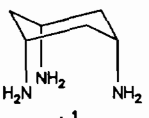
	x	y	z	U_{eq}
Zn(1)	3090(1)	9045(1)	0	29(1)
N(11)	4122(6)	10090(6)	377(4)	36(5)
N(12)	3866(6)	8529(6)	−114(4)	34(5)
N(13)	3515(6)	9631(7)	−825(4)	37(5)
N(21)	2305(7)	9554(7)	125(4)	37(6)
N(22)	2056(7)	7999(7)	−382(5)	37(6)
N(23)	2655(7)	8446(7)	827(4)	38(5)
C(11)	4891(8)	10398(8)	88(6)	37(3)
C(12)	5151(8)	9789(8)	74(6)	36(3)
C(13)	4683(8)	9072(8)	−321(5)	36(3)
C(14)	4667(8)	9389(8)	−908(6)	39(4)
C(15)	4377(8)	9988(8)	−927(6)	37(3)
C(16)	4864(8)	10664(8)	−513(6)	36(3)
C(21)	1786(8)	8075(8)	931(6)	36(3)
C(22)	1317(9)	7396(9)	508(6)	44(4)
C(23)	1288(8)	7698(8)	−91(6)	37(3)
C(24)	1020(9)	8329(8)	−81(6)	41(4)
C(25)	1490(8)	9005(8)	330(5)	37(3)
C(26)	1523(9)	8702(8)	932(6)	40(4)
Zn(2)	6667	3333	1425(1)	29(1)
N(31)	7519(6)	3227(7)	1972(4)	35(5)
N(41)	6568(7)	2373(6)	868(4)	35(5)
C(31)	7379(8)	3232(8)	2597(6)	36(3)
C(32)	7454(8)	4019(8)	2776(6)	37(3)
C(41)	6592(8)	2519(8)	239(6)	38(3)
C(42)	7398(8)	3230(9)	66(7)	43(4)
S(1)	3333	6667	873(3)	38(1)
O(1)	4119(8)	7277(8)	712(6)	86(4)
C(1)	3333	6667	1816(32)	169(24)
F(1)	3295(16)	7281(14)	1823(11)	214(10)
S(2)	0	0	2301(3)	38(1)
O(2)	−329(7)	−821(7)	2442(5)	65(3)
C(2)	0	0	1482(16)	82(10)
F(2)	445(9)	−294(9)	1326(6)	118(5)
S(3)	8545(2)	2089(2)	1295(2)	39(1)
O(31)	8278(9)	2512(9)	943(6)	90(4)
O(32)	8288(8)	2039(8)	1880(6)	89(4)
O(33)	9374(8)	2359(8)	1241(6)	86(4)
C(3)	7919(33)	892(28)	985(26)	186(16)
F(31)	7286(18)	829(16)	981(12)	222(11)
F(32)	8105(18)	615(17)	1390(14)	238(12)
F(33)	8350(17)	1025(16)	573(13)	224(11)
S(4)	−185(2)	4631(2)	1928(2)	38(1)
O(41)	−500(7)	4161(7)	2433(5)	67(3)
O(42)	−783(7)	4606(7)	1560(5)	66(3)
O(43)	437(7)	4558(7)	1665(5)	65(3)
C(4)	355(14)	5692(13)	2201(11)	84(6)
F(41)	662(9)	6177(9)	1768(6)	117(4)
F(42)	−177(9)	5834(9)	2445(7)	121(5)
F(43)	908(9)	5780(9)	2555(6)	118(5)

Results and discussion

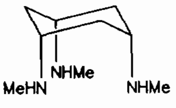
Reactions

The cyclohexane triamine ligand system was varied in order to change its steric properties as well as its electronic nature. Thus, in addition to the basic ligand

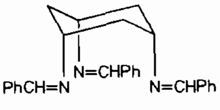
L^1, its methylamine analogue L^2 and its Schiff base with benzaldehyde L^3 were used.



L^1



L^2



L^3

The combinations of the ligands L^1 and L^2 with zinc halides $ZnCl_2$, $ZnBr_2$ and ZnI_2 in alcoholic solution were straightforward and produced the 1:1 complexes **1a**, **1b**, **1c** and **2a** in good yields as colourless precipitates of low solubility. Similarly, L^2 and $Zn(NO_3)_2$ led to precipitation of **2b**. A different behaviour was observed for $Zn(OAc)_2$ with which L^1 gave a 1:1 complex of rather high solubility which crystallized as the hydrate **1d**.

L^1ZnX_2
1a: $X=Cl$
1b: $X=Br$
1c: $X=I$

$L^1Zn(OAc)_2 \cdot H_2O$
1d

L^2ZnX_2
2a: $X=Cl$
2b: $X=NO_3$

$Zn(CF_3SO_3)_2$, $Zn(ClO_4)_2$, and $Zn(BF_4)_2$ were used as zinc salts of non-coordinating anions. Complexes of L^1 could be obtained with the former two. Irrespective of the reagent ratio these were only 2:1 complexes. Thus, $Zn(CF_3SO_3)_2$ produced **3a**. For $Zn(ClO_4)_2$ there were two different products depending on the reaction conditions. If the zinc salt and the ligand were allowed to diffuse into one another in methanol solution the normal 2:1 complex **3b** was obtained. However, upon mixing the reagents in water/methanol, the compound **3c** was formed which contains two additional equivalents of $HClO_4$ believed to be protonating the ligand. It is noteworthy that the complex $(L^1)_2Zn(NO_3)_2$ which was described by Wentworth [14] is not formed when a 1:1 stoichiometry of the reagents is applied. On the other hand we did not succeed in making 2:1 complexes using L^2.

$(L^1)_2ZnX_2$
3a: $X=CF_3SO_3$
3b: $X=ClO_4$

$(L^1H)_2Zn(ClO_4)_4$
3c

The ligand L^3 proved to be of little value in these studies. Its zinc complexes seem to be of little stability as they could neither be precipitated nor obtained pure by removal of the solvent. The ligand is decomposed in the presence of zinc salts in solution. This seems to be mainly due to zinc catalyzed solvolysis, as benzaldehyde could be isolated after reaction of L^3 with $Zn(BF_4)_2$.

One major goal of this study could not be reached, namely the unambiguous identification of a monofunctional tetrahedral LZnX complex by crystal structure determination. Neither of the compounds **1** or **2** could be obtained in the form of X-ray quality crystals. Two variations were sought to circumvene this problem. Firstly it was tried to enforce the all-axial geometry of the ligand in solution by using a trimethyl cyclohexane backbone. But the synthesis of 1,3,5-trimethyl cyclohexane 1,3,5-triamine according to the procedures of Rebek *et al.* [21] failed. Secondly it was hoped to obtain a complex cation $[LZnOH_2]^{2+}$ or $[LZnOH]^+$ from L^1 and L^2, respectively, and $Zn(ClO_4)_2 \cdot 6H_2O$. However this reaction which we performed successfully with pyrazolylborate [10] and tris-(benzimidazolylmethyl)amine ligands [22] did not take place here. Instead, under all conditions the 2:1 complexes were formed.

Spectra and constitutions

The IR spectra of the complexes (see 'Experimental') are in agreement with their given compositions as they show the typical amine N–H bands as well as the resonances of the anionic ligands in **1d**, **2b** and **3a–c** and the water molecule in **1d**. They give detailed information with respect to the monodentate nature [23] of the acetate ligands in **1d** and the presence of NH_3 groups [24] in **3c** due to their typical band positions. For the nitrate compound **2b** the strong ν(NO) band with two weak side bands does not allow an unambiguous statement about the bonding mode of the two NO_3^- ions [25].

The ^1H NMR spectra of the complexes (see 'Experimental') have very broad resonances with more or less resolved spin–spin coupling as a common feature. Variable temperature measurements for **1c**, **2b** and **3a** between −60 and +50 °C did not show any variation of these features thus confirming that ligand exchange or conformational movements are not responsible for them. There is a typical low field shift upon coordination which is most pronounced (*c.* 1 ppm) for the CH unit of the cyclohexane ring connected to the amine group. In all cases there is no indication of free ligands L in solution, and the small (i.e. unresolved) coupling between the cyclohexane CH_2 and CHN protons corresponds to the ring conformation imposed by coordination to the zinc ion. Compound **3c** shows a complex pattern for the CH resonances which yields no information, but a typical low field signal for the $-NH_3^+$ group. There is just one signal for the acetate groups in **1d** indicating only one bonding mode for them, and the bis-ligand complexes **3a** and **3b** show just one set of ligand signals confirming their symmetrical attachment.

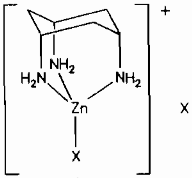
Most information can be drawn from the ^{13}C NMR spectra, see Table 2. The two resonances for L^1 and the three resonances for L^2 are all shifted to high field upon coordination. The magnitude of this shift ($CHN > CH_3 > CH_2$) is related to the distance from the coordination site. The resonances are all narrow, and if additional ligand L is added its resonances show up

TABLE 2. ^{13}C NMR data of the compounds

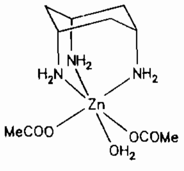
No.	Solvent	δ(CH)	δ(CH_2)	δ(X)
L^1	CD_3CN	47.9	48.9	
L^2	$CDCl_3$	33.6	55.7	39.6 (CH_3)
1a	DMSO-d_6	33.1	45.7	
1b	DMSO-d_6	32.5	45.0	
1c	DMSO-d_6	32.6	44.9	
1d	CD_3OD	34.4	46.7	23.1 (CH_3) 180.9 (COO)
2a	CD_3OD	30.1	55.5	35.2 (CH_3)
2b	DMSO-d_6	28.9	53.8	35.6 (CH_3)
3a	DMSO-d_6	34.0	43.4	120.8 (CF_3)
3b	DMSO-d_6	34.4 33.4^a	43.7 44.7^a	
3c	DMSO-d_6	34.6 33.6^a	43.9 44.8^a	

^{a}Signals of lower intensity.

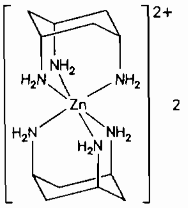
separately thus eliminating the possibility of fast ligand exchange. With the exception of **3b** and **3c** the ^{13}C NMR spectra confirm the symmetrical tridentate nature of L^1 and L^2. For **3c** two sets of two signals having roughly the intensity ratio 2:1 are in agreement with the bidentate nature of L^1 whose third amine group is protonated. A very similar spectrum is observed for **3b** which is unexpected according to its composition and its similarity with **3a**. We assume that **3b** is very sensitive to partial hydrolysis in the presence of water which could not be avoided in the NMR experiment, yielding some **3c** in solution. This is in agreement with the ease of formation of **3c** and its obvious stability in solution according to measurements of Schwarzenbach and Brauner [12].



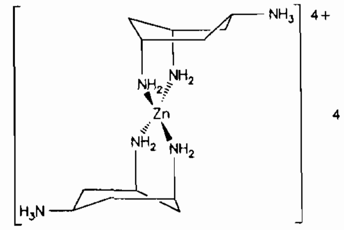
A



B



C



D

The spectra give unambiguous information with respect to the bonding mode of L^1 and L^2. In addition they confirm the attachment of both acetate groups and the water molecule in **1d**. Therefore they prove the structural type B for **1d** and the structural types C for **3a** and **3b** and D for **3c**. The physical properties of the remaining complexes (**1a**, **1b**, **1c**, **2a**, **2b**) allow the structural type A to be assigned to them. All five are only soluble in very polar solvents (water, DMSO, partly in methanol) supporting their ionic nature. Similarly they do not melt before they decompose at rather high temperatures. In these respects they differ significantly from **1d** for which we assume a molecular structure. Further support for structural type A comes from the EI mass spectrum of **1c** which shows the species $[L^1ZnI]^+$ as the ion with the highest mass. It must be said, however, that type A is disputable in the absence of a crystal structure determination. Alternative bonding modes with a molecular tetrahedral structure containing only bidentate L [8] or molecular five-coordinate species [26] are not completely unlikely. This holds especially for the nitrate compound **2b** whose IR data are not conclusive and which is reasonably soluble in methanol.

Structure determination

The bis-ligand complex **3a** yielded good crystals which were used to prove its octahedral nature. All crystallographic details are given in 'Experimental'. Figure 1 shows the molecular shape of the cation, Table 3 lists the pertinent structural data. There are two cations and four anions each per asymmetric unit in the rhombohedral unit cell. One of the cations and two of the anions have threefold crystallographic symmetry. There seems to be some disorder in the CF_3SO_3 anions, especially the two on special positions, which becomes obvious from the high thermal parameters and the spread in S–C (1.88–2.22 Å) and C–F distances (1.16–1.31 Å) while the S–O distances stay rather constant (1.41–1.45 Å).

The coordination of the zinc in both independent $(L^1)_2Zn$ cations is very close to ideally octahedral. All

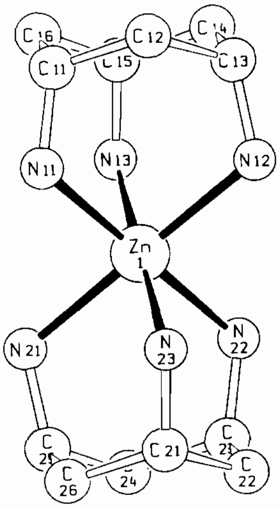


Fig. 1. One of the two crystallographically independent cations $(L^1)_2Zn$ in the solid state structure of **3a**.

TABLE 3. Bond lengths (Å) and angles (°) for **3a**

Zn1–N11	2.187(9)	N11–Zn1–N12	87.5(5)
Zn1–N12	2.182(15)	N11–Zn1–N13	87.4(4)
Zn1–N13	2.191(10)	N12–Zn1–N13	87.8(5)
Zn1–N21	2.192(16)	N21–Zn1–N22	87.3(5)
Zn1–N22	2.194(10)	N21–Zn1–N23	87.1(5)
Zn1–N23	2.206(10)	N22–Zn1–N23	87.1(4)
N11–C11	1.459(18)	N11–Zn1–N21	92.6(5)
N12–C13	1.470(15)	N11–Zn1–N23	93.1(4)
N13–C15	1.463(18)	N12–Zn1–N22	92.6(5)
N21–C25	1.468(16)	N12–Zn1–N23	92.2(5)
N22–C23	1.460(19)	N13–Zn1–N21	93.0(5)
N23–C21	1.474(18)	N13–Zn1–N22	92.4(4)
C–C(ring 1)	1.51±2(2)	N11–Zn1–N22	179.8(4)
C–C(ring 2)	1.53±2(2)	N12–Zn1–N21	179.2(4)
Zn2–N31	2.173(13)	N13–Zn1–N23	179.5(4)
Zn2–N41	2.195(12)	N31–Zn2–N31A	88.4(4)
N31–C31	1.500(17)	N41–Zn2–N41A	88.0(4)
N41–C41	1.508(17)	N31–Zn2–N41	91.6(5)
C–C(ring 3)	1.51±1(2)	N31–Zn2–N41A	92.1(4)
C–C(ring 4)	1.55±3(3)	N31–Zn2–N41B	179.6(4)

Zn–N distances are very similar (av. 2.192 Å in the first and 2.184 Å in the second cation), and they correspond to the normal value for octahedral zinc complexes [27]. The intraligand N–Zn–N angles are slightly below and the interligand N–Zn–N angles slightly above 90°, as is also usual for tridentate ligands, cf. the pyrazolylborate zinc complex [28]. We have described two L_2Zn complexes of tridentate ligands with a close relation to **3a**, namely for L = triazacyclononane [29] and L = tris(methylaminomethyl)ethane [8]. In both of them bond lengths and angles around the zinc show a similar distribution, but in **3a** the closest approximation to an ideal octahedron is realized.

The bond distances and angles in the cyclohexane part of the ligands in **3a** are normal. The cyclohexane ring is fixed in the chair conformation. Each separate Zn–N–C–C–C–N ring has the chair conformation as well. Thus, each L^1Zn unit has the adamantane structure. Although the octahedral geometry around zinc and the lengths of the Zn–N bonds induce strain into this structure, this can obviously be accommodated in a stable molecular unit with a satisfactory geometrical situation for all its constituents.

Conclusions

This paper has shown that 1:1 and 2:1 complexes of cyclohexane triamine ligands with zinc salts can be isolated. For one of the 2:1 complexes the crystal structure determination has proved the octahedral geometry around zinc. Chemical and physical evidence indicates that in the 1:1 complexes with zinc halides there is a tetrahedral coordination of one tridentate ligand and one halide ion. However, due to observations in this and previous investigations, a tetrahedral structure with only bidentate triamine ligands or an octahedral structure with one additional solvent ligand cannot be ruled out. Thus, even with these good chelating ligands zinc demonstrates its coordinative flexibility.

Supplementary material

All details of the crystal structure determination are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, quoting the depository no. CSD 320393, the authors and the journal citation.

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