1,4,7,10 – Tetraazacyclododecane Metal Complexes as Potent Promoters of Carboxyester Hydrolysis under Physiological Conditions

Supplementary Information

1. Crystal data and data collection parameters, atomic positional parameters with standard deviations, bond length, bond angles, torsion angles and hydrogen bonds of $[Zn_2L2]\mu$-$OH(ClO_4)_3 \cdot CH_3CN \cdot H_2O$.

Empirical formula ;C20 H42 N11 O2 Zn2, C2 H3 N, 3(Cl O4), H2O
Formula weight : 956.81
Crystal size : 0.20 x 0.12 x 0.06 mm
Crystal description : plate
Crystal colour : translucent colorless
Crystal system: Monoclinic
Space group : P 21/n

Unit cell dimensions	;a = 14.9051(8) A alpha = 90 deg.
	;b = 10.5525(6) A beta = 105.687(6) deg.
	;c = 24.4935(13) A gamma = 90 deg.

Volume ;3709.0(4) A^3

Z, Calculated density ;4, 1.713 Mg/m^3

Absorption coefficient ;1.592 mm^-1

F(000) ;1976

Data Collection ;

Measurement device type ;STOE-IPDS diffractometer

Measuremnet method ;rotation

Temperature ;173(1) K

Wavelength ;0.71073 A

Monochromator ; graphite

Theta range for data collection ;2.11 to 25.85 deg.

Index ranges ;-18<=h<=18, -12<=k<=12, -29<=l<=29

Reflections collected / unique ;32904 / 7132 [R(int) = 0.1253]

Reflections greater I>4\\s(I);3085

Absorption correction ;Empirical

Max. and min. transmission ;0.802 and 0.413

Refinement ;

Refinement method ;Full-matrix least-squares on F^2

Hydrogen treatment ;mixed

Data / restraints / parameters ;7132 / 0 / 490

Goodness-of-fit on F^2 ;0.803

Final R indices [I>2sigma(I)] ;R1 = 0.0597, wR2 = 0.1181

R indices (all data) ;R1 = 0.1459, wR2 = 0.1427
Absolute structure parameter ;

Largest diff. peak and hole ;0.916 and -0.692 e.A^-3

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zn(1)	2642(1)	2382(1)	-185(1)	47(1)
Zn(2)	3320(1)	411(1)	1060(1)	43(1)
O(1)	1211(3)	-2347(5)	-538(2)	52(2)
O(2)	3087(3)	967(5)	293(2)	44(2)
N(1)	2288(5)	1950(8)	-1065(3)	77(3)
N(2)	860(4)	1990(5)	-513(2)	42(2)
N(3)	2127(4)	4031(6)	61(3)	50(2)
N(4)	3746(5)	3461(8)	-300(4)	76(3)
N(5)	3345(5)	-1554(6)	1202(2)	54(2)
N(6)	4721(5)	373(8)	1498(3)	67(3)
N(7)	3101(5)	1550(6)	1682(2)	57(2)
N(8)	1648(4)	-300(6)	1143(2)	53(2)
N(9)	1086(4)	828(6)	316(2)	42(2)
N(10)	1028(4)	-180(5)	-566(2)	39(2)
N(11)	1417(4)	-1381(6)	299(3)	48(2)
C(1)	1425(6)	2546(10)	-1350(3)	73(4)
C(2)	670(6)	2038(7)	-1135(3)	49(3)
C(3)	549(5)	3101(7)	-234(3)	42(2)
C(4)	1120(5)	4254(6)	-237(3)	42(2)
C(5)	2717(6)	5093(8)	-39(4)	68(3)
C(6)	3733(6)	4606(11)	39(5)	94(4)
C(7)	3557(8)	3611(12)	-920(5)	100(5)
C(8)	3170(8)	2438(13)	-1220(5)	96(5)
C(9)	4326(6)	-1866(9)	1372(4)	69(3)
C(10)	4890(6)	-896(8)	1769(3)	62(3)
C(11)	4822(7)	1436(9)	1874(4)	74(3)
C(12)	4039(7)	1598(10)	2133(4)	80(4)
C(13)	2315(6)	1169(8)	1918(3)	54(3)
C(14)	1471(6)	793(9)	1470(3)	63(3)
C(15)	1832(6)	-1522(8)	1431(4)	63(3)
C(16)	2844(6)	-1827(8)	1633(3)	62(3)
C(17)	983(5)	833(6)	-240(3)	39(2)
C(18)	1209(5)	-1262(7)	-270(3)	43(2)
C(19)	1350(5)	-282(7)	556(3)	44(2)
C(20)	1038(5)	-2287(8)	-1146(3)	55(3)
N(21)	1853(8)	5074(12)	-2051(6)	138(6)
C(22)	2249(8)	5971(14)	-2053(5)	91(5)
C(23)	2741(8)	7151(10)	-2057(4)	86(4)
Cl(1)	-421(2)	268(2)	2595(1)	86(1)
O(4)	-315(7)	-118(8)	3159(4)	123(4)
O(5)	-1257(10)	-271(11)	2191(5)	188(7)
O(6)	-605(11)	1503(9)	2552(5)	223(7)
O(7)	295(10)	-50(20)	2445(5)	285(11)
Cl(2)	1207(2)	4595(2)	1526(1)	80(1)
O(8)	1258(10)	3870(8)	1994(3)	167(6)
O(9)	1070(8)	3835(9)	1054(3)	147(5)
O(10)	375(11)	5278(13)	1497(5)	212(7)
O(11)	1818(13)	5428(14)	1599(8)	278(10)
Cl(3)	3961(2)	-1630(2)	-449(1)	72(1)
O(12)	4617(6)	-2188(11)	-600(4)	152(5)
O(13)	3691(8)	-533(8)	-786(4)	157(5)
O(14)	4170(20)	-1533(15)	75(6)	430(20)
O(15)	3305(9)	-2340(30)	-520(14)	510(20)
O(3)	3379(8)	4225(8)	1315(4)	136(4)

Table 2. Bond lengths [A] and angles [deg].

Zn(1)-O(2)	1.902(5)
Zn(1)-N(1)	2.125(7)
Zn(1)-N(3)	2.058(6)
Zn(1)-N(4)	2.082(8)
Zn(2)-O(2)	1.909(5)
Zn(2)-N(5)	2.101(6)
Zn(2)-N(6)	2.074(8)
Zn(2)-N(7)	2.036(6)
Cl(1)-O(4)	1.408(10)
Cl(1)-O(5)	1.479(14)
Cl(1)-O(6)	1.330(10)
Cl(1)-O(7)	1.264(16)
Cl(2)-O(9)	1.377(8)
Cl(2)-O(10)	1.419(16)
Cl(2)-O(8)	1.363(8)
Cl(2)-O(11)	1.243(18)
Cl(3)-O(12)	1.279(10)
Cl(3)-O(13)	1.415(9)
Cl(3)-O(15)	1.21(2)
Cl(3)-O(14)	1.241(14)
O(1)-C(20)	1.442(9)
O(1)-C(18)	1.320(9)
O(2)-H(2O)	0.88(7)
N(1)-C(1)	1.432(12)

N(1)-C(8);1.552(15)
N(2)-C(3);1.493(9)
N(2)-C(17);1.380(8)
N(2)-C(2);1.473(9)
N(3)-C(5);1.485(11)
N(3)-C(4);1.500(10)
N(4)-C(6);1.469(15)
N(4)-C(7);1.476(15)
N(5)-C(9);1.446(12)
N(5)-C(16);1.477(10)
N(6)-C(11);1.433(12)
N(6)-C(10);1.486(12)
N(7)-C(13);1.495(11)
N(7)-C(12);1.530(12)
N(8)-C(14);1.468(11)
N(8)-C(19);1.385(9)
N(8)-C(15);1.460(11)
N(9)-C(17);1.329(9)
N(9)-C(19);1.322(10)
N(10)-C(17);1.347(8)
N(10)-C(18);1.340(9)
N(11)-C(18);1.349(10)
N(11)-C(19);1.336(10)
N(1)-H(1);0.9303
N(3)-H(3);0.9291
N(4)-H(4);0.9301
N(5)-H(5);0.9299
N(6)-H(6);0.9290
N(7)-H(7);0.9304
N(21)-C(22);1.116(19)
C(1)-C(2);1.467(13)
C(3)-C(4);1.486(10)
C(5)-C(6);1.561(13)
C(7)-C(8);1.475(18)
C(9)-C(10);1.503(12)
C(11)-C(12);1.481(15)
C(13)-C(14);1.482(12)
C(15)-C(16);1.490(13)
C(1)-H(1A);0.9889
C(1)-H(1B);0.9901
C(2)-H(2A);0.9897
C(2)-H(2B);0.9905
C(3)-H(3A);0.9896
C(3)-H(3B);0.9907
C(4)-H(4B);0.9916
C(4)-H(4A);0.9905
C(5)-H(5A);0.9903
C(5)-H(5B);0.9903
C(6)-H(6A);0.9888
C(6)-H(6B);0.9890
C(7)-H(7B);0.9909
C(7)-H(7A);0.9895
C(8)-H(8A);0.9883
C(8)-H(8B);0.9900
C(9)-H(9A);0.9913
C(9)-H(9B);0.9897
C(10)-H(10A);0.9903
C(10)-H(10B);0.9894
C(11)-H(11A);0.9900
C(11)-H(11B);0.9902
C(12)-H(12A);0.9894
C(12)-H(12B);0.9899
C(13)-H(13A);0.9899
C(13)-H(13B);0.9909
C(14)-H(14A);0.9889
C(14)-H(14B);0.9899
C(15)-H(15A);0.9906
C(15)-H(15B);0.9893
C(16)-H(16B);0.9906
C(16)-H(16A);0.9904
C(20)-H(20B);0.9789
C(20)-H(20C);0.9806
C(20)-H(20A);0.9802
C(22)-C(23);1.446(18)
C(23)-H(23B);0.9793
C(23)-H(23C);0.9786
C(23)-H(23A);0.9809
O(2)-Zn(1)-N(1);113.9(3)
O(2)-Zn(1)-N(3);125.4(2)
O(2)-Zn(1)-N(4);110.9(3)
N(1)-Zn(1)-N(3);117.9(3)
N(1)-Zn(1)-N(4);88.2(3)
N(3)-Zn(1)-N(4);87.0(3)
O(2)-Zn(2)-N(5);117.2(2)
O(2)-Zn(2)-N(6);113.9(3)
O(2)-Zn(2)-N(7);122.2(2)
N(5)-Zn(2)-N(6);85.7(3)
N(5)-Zn(2)-N(7);117.2(2)
N(6)-Zn(2)-N(7);88.1(3)
O(6)-Cl(1)-O(7);114.2(12)
O(4)-Cl(1)-O(7);109.2(8)
O(4)-Cl(1)-O(5);113.3(7)
O(4)-Cl(1)-O(6);109.1(7)
O(5)-Cl(1)-O(6);101.9(8)
O(5)-Cl(1)-O(7);109.2(9)
O(8)-Cl(2)-O(10);100.2(8)
O(8)-Cl(2)-O(9);110.0(5)
O(9)-Cl(2)-O(11);118.0(10)
O(8)-Cl(2)-O(11);113.8(10)
O(9)-Cl(2)-O(10);108.9(7)
O(10)-Cl(2)-O(11);104.1(10)
O(12)-Cl(3)-O(15);109.0(14)
O(12)-Cl(3)-O(13);109.1(7)
O(12)-Cl(3)-O(14);109.8(14)
O(13)-Cl(3)-O(15);109.4(15)
O(14)-Cl(3)-O(15);100(2)
O(13)-Cl(3)-O(14);119.2(9)
C(18)-O(1)-C(20);116.8(6)
Zn(1)-O(2)-Zn(2);141.9(3)
Zn(2)-O(2)-H(2O);112(5)
Zn(1)-O(2)-H(2O);104(5)
Zn(1)-N(1)-C(8);100.5(6)
C(1)-N(1)-C(8);116.3(8)
Zn(1)-N(1)-C(1);110.1(5)

C(3)-N(2)-C(17);119.3(5)
C(2)-N(2)-C(17);119.6(5)
C(2)-N(2)-C(3);116.7(5)
Zn(1)-N(3)-C(4);113.2(4)
Zn(1)-N(3)-C(5);107.8(5)
C(4)-N(3)-C(5);111.1(6)
C(6)-N(4)-C(7);117.7(9)
Zn(1)-N(4)-C(7);105.1(7)
Zn(1)-N(4)-C(6);104.0(6)
Zn(2)-N(5)-C(16);108.8(5)
C(9)-N(5)-C(16);114.7(6)
Zn(2)-N(5)-C(9);104.1(5)
Zn(2)-N(6)-C(10);105.9(5)
Zn(2)-N(6)-C(11);103.5(6)
C(10)-N(6)-C(11);116.3(7)
Zn(2)-N(7)-C(12);105.0(5)
C(12)-N(7)-C(13);112.8(6)
Zn(2)-N(7)-C(13);115.6(5)
C(14)-N(8)-C(15);117.9(6)
C(14)-N(8)-C(19);120.1(6)
C(15)-N(8)-C(19);118.6(6)
C(17)-N(9)-C(19);113.4(6)
C(17)-N(10)-C(18);113.0(5)
C(18)-N(11)-C(19);112.4(6)
C(8)-N(1)-H(1);109.78
Zn(1)-N(1)-H(1);109.86
C(1)-N(1)-H(1);109.80
C(4)-N(3)-H(3);108.22
C(5)-N(3)-H(3);108.15
Zn(1)-N(3)-H(3);108.19
Zn(1)-N(4)-H(4);109.88
C(6)-N(4)-H(4);109.86
C(7)-N(4)-H(4);109.88
C(9)-N(5)-H(5);109.72
Zn(2)-N(5)-H(5);109.70
C(16)-N(5)-H(5);109.73
C(11)-N(6)-H(6);110.23
C(10)-N(6)-H(6);110.32
Zn(2)-N(6)-H(6);110.21
Zn(2)-N(7)-H(7);107.70
C(13)-N(7)-H(7);107.64
C(12)-N(7)-H(7);107.65
N(1)-C(1)-C(2);109.9(7)
N(2)-C(2)-C(1);115.6(7)
N(2)-C(3)-C(4);113.1(6)
N(3)-C(4)-C(3);111.6(6)
N(3)-C(5)-C(6);109.2(7)
N(4)-C(6)-C(5);111.2(8)
N(4)-C(7)-C(8);111.3(10)
N(1)-C(8)-C(7);113.6(10)
N(5)-C(9)-C(10);112.1(7)
N(6)-C(10)-C(9);109.1(7)
N(6)-C(11)-C(12);114.0(8)
N(7)-C(12)-C(11);111.0(7)
N(7)-C(13)-C(14);112.5(6)
N(8)-C(14)-C(13);111.9(7)
N(8)-C(15)-C(16);113.1(7)
N(5)-C(16)-C(15);112.5(6)
N(2)-C(17)-N(10);115.9(6)
N(2)-C(17)-N(9);117.6(6)
N(9)-C(17)-N(10);126.4(6)
O(1)-C(18)-N(10);119.8(6)
O(1)-C(18)-N(11);113.7(6)
N(10)-C(18)-N(11);126.5(7)
N(9)-C(19)-N(11);127.6(7)
N(8)-C(19)-N(9);116.6(6)
N(8)-C(19)-N(11);115.7(7)
C(2)-C(1)-H(1A);109.75
C(2)-C(1)-H(1B);109.68
N(1)-C(1)-H(1B);109.68
N(1)-C(1)-H(1A);109.75
H(1A)-C(1)-H(1B);108.11
N(2)-C(2)-H(2B);108.41
N(2)-C(2)-H(2A);108.33
H(2A)-C(2)-H(2B);107.43
C(1)-C(2)-H(2A);108.39
C(1)-C(2)-H(2B);108.39
N(2)-C(3)-H(3A);108.94
C(4)-C(3)-H(3B);109.00
N(2)-C(3)-H(3B);109.01
C(4)-C(3)-H(3A);109.01
H(3A)-C(3)-H(3B);107.68
C(3)-C(4)-H(4B);109.24
H(4A)-C(4)-H(4B);108.02
C(3)-C(4)-H(4A);109.33
N(3)-C(4)-H(4A);109.33
N(3)-C(4)-H(4B);109.23
N(3)-C(5)-H(5A);109.85
N(3)-C(5)-H(5B);109.78
C(6)-C(5)-H(5A);109.86
C(6)-C(5)-H(5B);109.81
H(5A)-C(5)-H(5B);108.29
N(4)-C(6)-H(6B);109.45
H(6A)-C(6)-H(6B);108.02
C(5)-C(6)-H(6A);109.37
C(5)-C(6)-H(6B);109.32
N(4)-C(6)-H(6A);109.39
N(4)-C(7)-H(7B);109.45
C(8)-C(7)-H(7A);109.41
C(8)-C(7)-H(7B);109.29
H(7A)-C(7)-H(7B);107.97
N(4)-C(7)-H(7A);109.40
N(1)-C(8)-H(8B);108.82
C(7)-C(8)-H(8A);108.87
N(1)-C(8)-H(8A);108.88
H(8A)-C(8)-H(8B);107.74
C(7)-C(8)-H(8B);108.81
N(5)-C(9)-H(9A);109.14
N(5)-C(9)-H(9B);109.30
C(10)-C(9)-H(9B);109.23
H(9A)-C(9)-H(9B);107.92
C(10)-C(9)-H(9A);109.05
C(9)-C(10)-H(10B);109.88
H(10A)-C(10)-H(10B);108.33

C(9)-C(10)-H(10A);109.87
N(6)-C(10)-H(10A);109.76
N(6)-C(10)-H(10B);109.89
N(6)-C(11)-H(11B);108.67
H(11A)-C(11)-H(11B);107.62
C(12)-C(11)-H(11A);108.84
C(12)-C(11)-H(11B);108.80
N(6)-C(11)-H(11A);108.68
C(11)-C(12)-H(12B);109.37
H(12A)-C(12)-H(12B);108.07
N(7)-C(12)-H(12B);109.47
C(11)-C(12)-H(12A);109.44
N(7)-C(12)-H(12A);109.41
N(7)-C(13)-H(13A);109.11
N(7)-C(13)-H(13B);109.16
H(13A)-C(13)-H(13B);107.83
C(14)-C(13)-H(13B);109.07
C(14)-C(13)-H(13A);109.07
N(8)-C(14)-H(14B);109.17
N(8)-C(14)-H(14A);109.32
H(14A)-C(14)-H(14B);107.94
C(13)-C(14)-H(14A);109.21
C(13)-C(14)-H(14B);109.25
C(16)-C(15)-H(15A);108.93
C(16)-C(15)-H(15B);109.02
H(15A)-C(15)-H(15B);107.65
N(8)-C(15)-H(15B);109.09
N(8)-C(15)-H(15A);108.91
N(5)-C(16)-H(16B);109.09
N(5)-C(16)-H(16A);109.15
H(16A)-C(16)-H(16B);107.80
C(15)-C(16)-H(16B);109.13
C(15)-C(16)-H(16A);109.08
O(1)-C(20)-H(20C);109.45
O(1)-C(20)-H(20B);109.39
H(20B)-C(20)-H(20C);109.52
H(20A)-C(20)-H(20B);109.60
H(20A)-C(20)-H(20C);109.47
O(1)-C(20)-H(20A);109.41
N(21)-C(22)-C(23);178.6(15)
C(22)-C(23)-H(23C);109.50
H(23A)-C(23)-H(23C);109.54
H(23B)-C(23)-H(23C);109.48
H(23A)-C(23)-H(23B);109.43
C(22)-C(23)-H(23A);109.44
C(22)-C(23)-H(23B);109.44

Symmetry transformations used to generate equivalent atoms:

Table 3. Anisotropic displacement parameters (A^2 x 10^3). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]
;U11 ;U22 ;U33 ;U23 ;U13 ;U12

Zn(1);37(1);55(1);50(1);21(1);12(1);6(1)
Zn(2);40(1);48(1);37(1);9(1);7(1);1(1)
O(1);53(3);34(3);64(3);-1(3);5(2);2(3)
O(2);52(3);46(3);38(3);10(2);17(2);18(2)
N(1);78(5);107(6);64(4);42(4);48(4);58(5)
N(2);53(4);35(3);37(3);-1(2);10(3);-2(3)
N(3);47(4);50(4);49(3);5(3);7(3);-5(3)
N(4);38(4);70(5);123(7);49(5);28(4);9(4)
N(5);58(4);65(4);35(3);3(3);8(3);18(4)
N(6);57(4);87(5);56(4);6(4);12(3);-20(4)
N(7);84(5);43(4);41(3);-2(3);14(3);-13(3)
N(8);51(4);55(4);49(3);16(3);9(3);-7(3)
N(9);43(3);46(4);36(3);2(3);9(3);-6(3)
N(10);34(3);34(3);45(3);-2(3);4(3);-5(3)
N(11);42(4);44(4);52(4);9(3);2(3);-10(3)
C(1);88(7);93(7);42(4);11(5);22(4);-3(6)
C(2);68(5);37(4);34(4);1(3);-1(4);2(4)
C(3);42(4);43(4);42(4);0(3);11(3);-3(3)
C(4);37(4);39(4);49(4);2(3);10(3);2(3)
C(5);50(5);46(5);99(7);17(5);4(5);-9(4)
C(6);43(5);81(7);149(10);52(8);9(6);-20(6)
C(7);102(9);103(9);124(10);71(8);78(8);34(7)
C(8);94(8);120(10);96(7);57(8);64(7);50(8)
C(9);66(6);83(6);53(5);3(5);10(4);15(5)
C(10);51(5);80(6);46(4);15(4);0(4);21(5)
C(11);64(6);65(6);80(6);20(5);-2(5);-14(5)
C(12);103(8);75(7);50(5);-4(5);1(5);-4(6)
C(13);63(5);61(5);38(4);9(4);13(4);26(4)
C(14);54(5);91(7);50(5);5(4);23(4);17(5)
C(15);69(6);62(5);54(5);19(4);12(4);-10(5)
C(16);77(6);49(5);57(5);13(4);11(4);-4(5)
C(17);29(4);36(4);52(4);0(3);9(3);-10(3)
C(18);30(4);39(4);55(4);0(3);3(3);-7(3)
C(19);35(4);43(4);51(4);8(4);7(3);-8(4)
C(20);51(5);46(5);63(5);-13(4);5(4);7(4)
N(21);84(8);101(9);217(14);31(9);18(8);-4(7)
C(22);58(7);100(9);103(8);19(7);1(6);13(7)
C(23);90(7);82(7);86(7);2(6);26(6);2(6)
Cl(1);128(2);46(1);104(2);-2(1);63(2);-3(2)
O(4);177(9);114(7);104(6);-1(5);84(6);-4(6)
O(5);277(15);162(10);149(9);-94(8);100(9);-131(10)
O(6);318(17);83(7);155(9);-44(6);-128(10);44(8)
O(7);218(13);530(30);157(10);189(15);136(10);
210(17)
Cl(2);124(2);41(1);56(1);-7(1);-9(1);1(2)
O(8);335(16);88(6);68(5);13(4);39(7);83(8)
O(9);259(12);129(7);59(4);-41(5);53(6);-64(8)
O(10);265(16);171(11);151(10);-11(8);-
29(9);117(12)
O(11);310(20);183(12);390(20);
-141(15);179(18);-189(14)
Cl(3);83(2);63(1);89(2);28(1);54(1);26(1)

O(12);137(7);213(11);129(7);78(7);75(6);118(8)
O(13);237(11);78(6);181(9);70(6);101(9);79(7)
O(14);1030(60);192(14);118(9);29(10);260(20);2
30(30)
O(15);90(9);570(40);840(50);620(40);62(17);
17(14)
O(3);199(10);90(6);101(6);6(5);11(6);5(6)

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).
;x ;y ;z ;U(eq)

H(1);2237;1077;-1117;93
H(1A);1475;3472;-1287;88
H(1B);1286;2389;-1763;88
H(2A);107;2562;-1287;59
H(2B);525;1169;-1286;59
H(2O);3390(50);510(70);100(30);53
H(3);2187;3983;448;60
H(3A);580;2877;163;51
H(3B);-110;3291;-431;51
H(4);4304;3028;-158;91
H(4A);1062;4511;-634;51
H(4B);880;4956;-47;51
H(5);3056;-1971;866;64
H(5A);2464;5428;-428;82
H(5B);2716;5787;233;82
H(6);5087;483;1249;81
H(6A);4020;4416;444;113
H(6B);4106;5278;-77;113
H(7);2974;2361;1532;68
H(7A);4142;3833;-1015;120
H(7B);3109;4314;-1049;120
H(8A);3013;2593;-1633;115
H(8B);3654;1770;-1129;115
H(9A);4410;-2704;1562;82
H(9B);4559;-1929;1031;82
H(10A);5561;-1108;1855;74
H(10B);4709;-892;2129;74
H(11A);5407;1335;2180;88
H(11B);4881;2215;1661;88
H(12A);4062;919;2415;96
H(12B);4103;2422;2333;96
H(13A);2158;1886;2136;65
H(13B);2517;450;2183;65
H(14A);1258;1517;1211;76
H(14B);967;578;1647;76
H(15A);1565;-1517;1760;75
H(15B);1513;-2196;1169;75
H(16A);2918;-2736;1736;75

H(16B);3127;-1327;1979;75
H(20A);424;-1909;-1312;67
H(20B);1519;-1768;-1241;67
H(20C);1053;-3145;-1297;67
H(23A);2306;7792;-2267;103
H(23B);3241;7021;-2241;103
H(23C);3008;7439;-1667;103

Table 5. Torsion angles [deg]

N(1)-Zn(1)-O(2)-Zn(2);	-164.3(4)
N(3)-Zn(1)-O(2)-Zn(2);	-3.6(6)
N(4)-Zn(1)-O(2)-Zn(2);	98.0(5)
O(2)-Zn(1)-N(1)-C(1);	136.5(6)
O(2)-Zn(1)-N(1)-C(8);	-100.2(6)
N(3)-Zn(1)-N(1)-C(1);	-25.8(7)
N(3)-Zn(1)-N(1)-C(8);	97.5(6)
N(4)-Zn(1)-N(1)-C(1);	-111.4(7)
N(4)-Zn(1)-N(1)-C(8);	11.8(7)
O(2)-Zn(1)-N(3)-C(4);	-116.2(5)
O(2)-Zn(1)-N(3)-C(5);	120.5(5)
N(1)-Zn(1)-N(3)-C(4);	43.8(6)
N(1)-Zn(1)-N(3)-C(5);	-79.5(6)
N(4)-Zn(1)-N(3)-C(4);	130.2(5)
N(4)-Zn(1)-N(3)-C(5);	6.9(6)
O(2)-Zn(1)-N(4)-C(6);	-107.1(6)
O(2)-Zn(1)-N(4)-C(7);	128.5(6)
N(1)-Zn(1)-N(4)-C(6);	137.9(7)
N(1)-Zn(1)-N(4)-C(7);	13.6(7)
N(3)-Zn(1)-N(4)-C(6);	19.8(6)
N(3)-Zn(1)-N(4)-C(7);	-104.5(7)

N(5)-Zn(2)-O(2)-Zn(1);	156.9(4)
N(6)-Zn(2)-O(2)-Zn(1);	-105.3(5)
N(7)-Zn(2)-O(2)-Zn(1);	-1.7(6)
O(2)-Zn(2)-N(5)-C(9);	99.6(5)
O(2)-Zn(2)-N(5)-C(16);	-137.8(4)
N(6)-Zn(2)-N(5)-C(9);	-15.2(5)
N(6)-Zn(2)-N(5)-C(16);	107.4(5)
N(7)-Zn(2)-N(5)-C(9);	-100.8(5)
N(7)-Zn(2)-N(5)-C(16);	21.8(6)
O(2)-Zn(2)-N(6)-C(10);	-130.4(5)
O(2)-Zn(2)-N(6)-C(11);	106.8(6)
N(5)-Zn(2)-N(6)-C(10);	-12.5(5)
N(5)-Zn(2)-N(6)-C(11);	-135.3(6)
N(7)-Zn(2)-N(6)-C(10);	105.0(5)
N(7)-Zn(2)-N(6)-C(11);	-17.8(6)
O(2)-Zn(2)-N(7)-C(12);	-123.4(5)
O(2)-Zn(2)-N(7)-C(13);	111.5(5)
N(5)-Zn(2)-N(7)-C(12);	78.1(6)
N(5)-Zn(2)-N(7)-C(13);	-47.0(6)
N(6)-Zn(2)-N(7)-C(12);	-6.1(5)
N(6)-Zn(2)-N(7)-C(13);	-131.2(5)
C(20)-O(1)-C(18)-N(10);	1.6(10)
C(20)-O(1)-C(18)-N(11);	-177.1(6)
Zn(1)-N(1)-C(8)-C(7);	-37.6(10)
C(1)-N(1)-C(8)-C(7);	81.3(11)
C(8)-N(1)-C(1)-C(2);	-176.7(8)
Zn(1)-N(1)-C(1)-C(2);	-63.2(8)
C(17)-N(2)-C(3)-C(4);	131.7(7)
C(2)-N(2)-C(3)-C(4);	-71.6(8)
C(2)-N(2)-C(17)-N(9);	-175.3(7)
C(3)-N(2)-C(17)-N(9);	-19.3(10)
C(3)-N(2)-C(2)-C(1);	93.3(9)
C(2)-N(2)-C(17)-N(10);	7.6(10)
C(3)-N(2)-C(17)-N(10);	163.6(6)
C(17)-N(2)-C(2)-C(1);	-110.1(8)
C(5)-N(3)-C(4)-C(3);	169.0(6)
Zn(1)-N(3)-C(4)-C(3);	47.6(7)
Zn(1)-N(3)-C(5)-C(6);	-31.1(8)
C(4)-N(3)-C(5)-C(6);	-155.7(7)
Zn(1)-N(4)-C(6)-C(5);	-42.5(9)
Zn(1)-N(4)-C(7)-C(8);	-38.6(11)
C(6)-N(4)-C(7)-C(8);	-153.8(9)
C(7)-N(4)-C(6)-C(5);	73.2(11)
Zn(2)-N(5)-C(16)-C(15);	65.6(7)
C(9)-N(5)-C(16)-C(15);	-178.4(7)
C(16)-N(5)-C(9)-C(10);	-77.4(9)
Zn(2)-N(5)-C(9)-C(10);	41.3(7)
Zn(2)-N(6)-C(11)-C(12);	40.5(9)
C(11)-N(6)-C(10)-C(9);	151.9(8)
Zn(2)-N(6)-C(10)-C(9);	37.6(8)
C(10)-N(6)-C(11)-C(12);	-75.2(10)
C(12)-N(7)-C(13)-C(14);	-164.7(7)
Zn(2)-N(7)-C(12)-C(11);	29.2(9)
C(13)-N(7)-C(12)-C(11);	156.0(7)
Zn(2)-N(7)-C(13)-C(14);	-43.8(8)
C(14)-N(8)-C(15)-C(16);	-98.5(8)
C(15)-N(8)-C(19)-N(9);	172.2(7)

C(15)-N(8)-C(19)-N(11); -11.6(10)
C(19)-N(8)-C(14)-C(13); -133.0(7)
C(15)-N(8)-C(14)-C(13); 68.0(9)
C(14)-N(8)-C(19)-N(9); 13.4(10)
C(19)-N(8)-C(15)-C(16); 102.2(8)
C(14)-N(8)-C(19)-N(11); -170.4(7)
C(19)-N(9)-C(17)-N(2); -169.6(7)
C(19)-N(9)-C(17)-N(10); 7.2(11)
C(17)-N(9)-C(19)-N(11); -8.0(11)
C(17)-N(9)-C(19)-N(8); 167.7(7)
C(18)-N(10)-C(17)-N(2); 175.9(6)
C(17)-N(10)-C(18)-N(11); -6.0(11)
C(18)-N(10)-C(17)-N(9); -1.0(11)
C(17)-N(10)-C(18)-O(1); 175.4(7)
C(18)-N(11)-C(19)-N(9); 2.3(11)
C(19)-N(11)-C(18)-N(10); 5.4(11)
C(18)-N(11)-C(19)-N(8); -173.4(6)
C(19)-N(11)-C(18)-O(1); -175.9(6)
N(1)-C(1)-C(2)-N(2); 48.5(10)
N(2)-C(3)-C(4)-N(3); -59.2(8)
N(3)-C(5)-C(6)-N(4); 51.5(11)
N(4)-C(7)-C(8)-N(1); 54.7(13)
N(5)-C(9)-C(10)-N(6); -55.7(9)
N(6)-C(11)-C(12)-N(7); -49.6(11)
N(7)-C(13)-C(14)-N(8); 60.9(9)
N(8)-C(15)-C(16)-N(5); -44.8(9)

Symmetry transformations used to generate equivalent atoms:

Table 6. Hydrogen-bonds [A and deg.].

D-H...A;d(D-H);d(H...A);d(D...A);<(DHA)

O(2)-H(2O)...O(13); 0.88(7); 2.58(7); 3.403(11); 156(6)
O(2)-H(2O)...O(14); 0.88(7); 2.46(8); 3.21(2); 144(6)
N(3)-H(3)...O(3); 0.9291; 2.3856; 3.140(12); 138.19
N(3)-H(3)...O(9); 0.9291; 2.5171; 3.242(12); 135.11
N(4)-H(4)...O(12)#1; 0.9301; 2.2813; 3.116(13); 149.04
N(5)-H(5)...N(11); 0.9299; 2.5396; 3.122(9); 120.99
N(6)-H(6)...O(12)#1; 0.9290; 2.5175; 3.264(13); 137.57
N(6)-H(6)...O(13)#1; 0.9290; 2.3924; 3.302(14); 166.29
N(7)-H(7)...O(3); 0.9304; 2.1655; 3.025(11); 153.12
C(1)-H(1B)...O(5)#2; 0.9901; 2.4641; 3.129(15); 124.14
C(2)-H(2A)...O(10)#3; 0.9897; 2.4034; 3.238(16); 141.66
C(2)-H(2B)...N(10); 0.9905; 2.2324; 2.702(9); 107.61
C(3)-H(3A)...O(9); 0.9896; 2.3359; 3.135(10); 137.26
C(3)-H(3A)...N(9); 0.9896; 2.2873; 2.761(9); 108.21
C(4)-H(4A)...O(10)#3; 0.9905; 2.5801; 3.319(15); 131.35
C(6)-H(6A)...O(3); 0.9888; 2.5704; 3.332(15); 133.75
C(8)-H(8B)...O(13); 0.9900; 2.5671; 3.334(16); 134.24
C(9)-H(9A)...O(6)#4; 0.9913; 2.5479; 3.290(15); 131.55
C(9)-H(9B)...O(14); 0.9897; 2.2934; 3.142(18); 143.12
C(13)-H(13A)...O(8); 0.9899; 2.4600; 3.286(14); 140.68
C(14)-H(14A)...O(9); 0.9889; 2.4802; 3.372(13); 149.84
C(14)-H(14A)...N(9); 0.9889; 2.2574; 2.728(9); 107.85
C(14)-H(14B)...O(7); 0.9899; 2.5143; 3.440(17); 155.49
C(15)-H(15B)...N(11); 0.9893; 2.2663; 2.677(12); 103.54

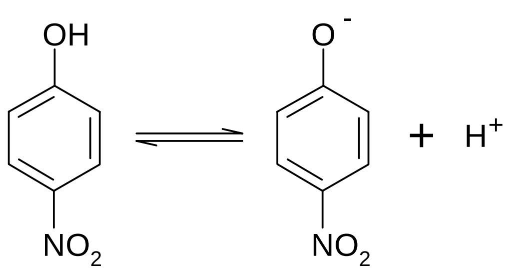
C(16)-H(16A)...O(11)#5; 0.9904; 2.5014; 3.266(18); 133.80
C(16)-H(16B)...O(8)#4; 0.9906; 2.4422; 3.348(10); 151.76
C(23)-H(23A)...O(6)#3; 0.9809; 2.5518; 3.396(19); 144.24
C(23)-H(23B)...O(5)#6; 0.9793; 2.5433; 3.324(17); 136.60

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z #2 -x,-y,-z #3 -x,-y+1,-z
#4 1/2-x,1/2+y-1,1/2-z #5 x,y-1,z #6 1/2+x,1/2-y,1/2+z-1

2. Calculation of the Molar Extinction Coefficients for *para*-nitrophenolate

The hydrolysis of 4-nitrophenyl acetate (NA) releases *p*-nitrophenolate as a product which can be detected spectrophotometrically. The molar extinction coefficient of the nitrophenol anion varies due to the protonation equilibrium, thus due to the pH value and the used buffer system. The molar extinction coefficient was determined experimentally for the pH range 7 to 9 in a buffer system TRIS/HCl (20-80 mM).

For the protonation equilibrium and its equilibrium constant K_a applies:



(HNP) (NP^-) (**1**)

$$K_a = \frac{[NP^-]\,[H^+]}{[HNP]} \qquad (\mathbf{2})$$

According to the *Lambert-Beer* law the absorption in diluted solution is:

$$\text{Abs} = \varepsilon_{obs}\, d\, [HNP]^{total} = \varepsilon_{NP}\, d\, [NP^-] \qquad (\mathbf{3})$$

where ε_{obs} is the measured extinction coefficient of HNP, ε_{NP} is the extinction coefficient of the *p*-nitrophenolate ion and d the thickness of the cell. Equations **(2)** and **(3)** give equation **(4)** which describes the relationship between the molar extinction coefficient and the pH value.

$$\varepsilon_{obs} = \frac{\varepsilon_{NP}\, K_a}{K_a + [H^+]} \qquad (\mathbf{4})$$

Plots of $1/\varepsilon_{obs}$ versus $[H^+]$ allow the determination of the molar extinction coefficient of the *p*-nitrophenolate for various pH values and various buffer systems. In the pH range of 7 to 9 for the buffer system TRIS/HCl the respective ε_{obs} values were obtained with a regression coefficient of $R^2 > 0.9991$ using a dilution series ($c = 10^{-4}$ to $5 \cdot 10^{-7}$ mol L^{-1} *p*-nitrophenol). The ε_{obs} values for 400 nm are summarised in Table 7.

pH [a]	ε_{obs} at 400 nm [mol^{-1} L cm^{-1}]
7.01	7805
7.04	8201
7.21	9938
7.28	10628
7.50	12665
7.81	15119
8.11	16581
8.53	17602
8.75	17911
9.01	18097

[a] Δ pH = ± 0.005

Table 7: ε_{obs}-values for *p*-nitrophenolate at 400 nm (25 °C, 50 mM TRIS/HCl).

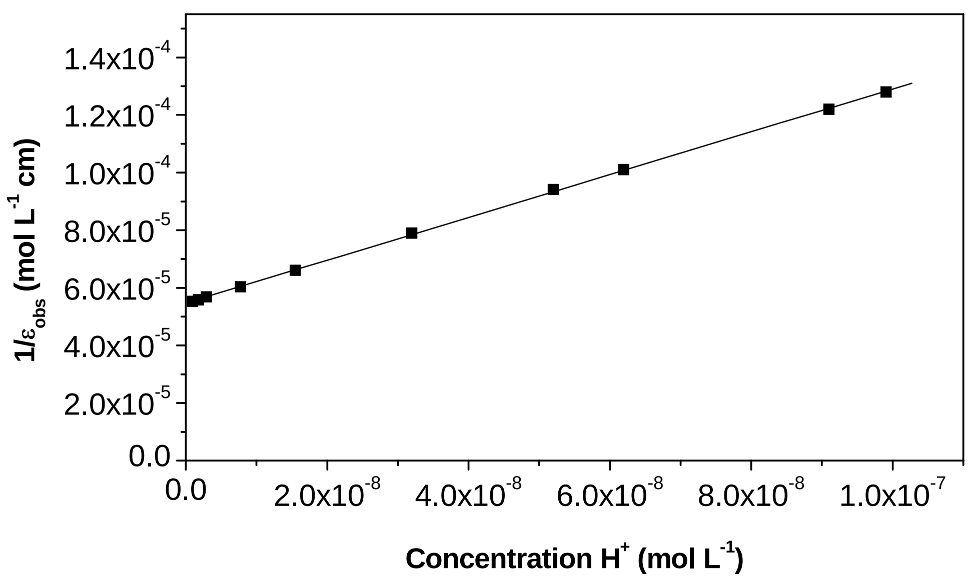


Figure 1: Calculation of the molar extinction coefficient for *p*-nitrophenolate at 400 nm (25 °C, 50 mM TRIS/HCl).

From the slope, respectively the axis segment we can calculate by using equation **(4)** the equilibrium constant (pK_a = 7.14 ± 0.01) as well as the molar extinction coefficient at 400 nm ($\varepsilon_{NP,\,400nm}$ = 18279 mol^{-1} L cm^{-1}). The value of the equilibrium constant calculated this way corresponds to the value from literature[1]. Variations in the buffer concentration (TRIS/HCl 20 and 80 mM) or in the ionic strength show no significant changes in the molar extinction coefficient. Changes in the region of $\Delta\varepsilon_{NP} \approx \pm 70$ mol^{-1} L cm^{-1} were detected.

3. Calculation of the spontaneous hydrolysis of 4-nitrophenyl acetate (NA)

The nucleophilic attack of OH^- in the used solvent system competes with the metal catalyzed hydrolysis of NA. This spontaneous hydrolysis has to be taken into account when analyzing the reaction kinetics. The spontaneous hydrolysis is a bimolecular reaction, described by equation **(5)**:

$$v = k_{x+y}\,[OH^-]^x\,[\text{Ester}]^y \qquad (5)$$

Under the given reaction conditions the velocity of reaction ν is directly proportional to the concentration of the used ester and the concentration of the hydroxide ions. Therefore the spontaneous hydrolysis shows second-order kinetics, with each reactant having a first order dependence. For a constant pH value equation **(5)** becomes:

$$v = \frac{d(\text{Abs})}{d(\text{t})\ \varepsilon_{obs}} = k'_{obs}\,[\text{Ester}] = (k_{OH}\,[OH^-] + k_0)\,[\text{Ester}] \qquad (6)$$

$$k'_{obs} = k_0 + k_{OH}\,[OH^-] \qquad (7)$$

Equation **(7)** shows the k'_{obs}-value as an additive value. The k_{OH} value is a second-order velocity constant describing the nucleophilic attack of the OH^- ions. The k_0 value is a first-order constant describing the solvolysis of the ester due to solvent molecules (e.g. water or organic additives).

The use of known values from literature for the spontaneous hydrolysis is not possible, as these constants depend on the reaction conditions (e.g. the type of buffer system used, the ionic strength, the presence of organic additives etc)[2].

The k'_{obs} value was determined by the initial slope method at constant pH with various concentrations of NA ([NA] = 2 to 5 mM). The results are presented in **Table 8.**

---

[1] a) J.A. Dean, Lange's *Handbook of Chemistry*, McGraw-Hill, New York, **1973**, *Vol.11*, Chapter 5; b) Robinson, R.A.; Briggs, A.T. *Trans. Faraday Soc*. **1955**, *51*, 901 (pK_a = 7.149 at 25 ºC).

[2] a) J. F. Kirsch, W. P. Jencks, *J. Am. Chem. Soc*. **1964**, *86*, 837-846; b) T. C. Bruice, C. L. Schmir, *J. Am. Chem. Soc*. **1957**, *79*, 1663-1667; c) W. P. Jencks, M. Gilchrist, *J. Am. Chem. Soc*. **1968**, *90*, 2622-2637

pH[a]	7.00[c]	7.20	7.34	7.52	7.82	7.93	8.00[c]	8.23	8.51
k'_{obs} [10^{-6} s^{-1}][b]	1.50	1.87	2.46	3.30	6.08	7.32	8.94	15.17	27.02

[a] Δ pH = ± 0.005; [b] 25.0 ± 0.1 °C, 50 mM TRIS/HCl, 10 % CH_3CN , Δ k'_{obs} = ± 2.0 · 10^{-8} s^{-1};
[c] I = 0 to 50 mM NaCl

Table 8: k_{obs} values for the spontaneous hydrolysis of NA

From the plot of k'_{obs} versus [OH^-] and equation **(7)** the following results were obtained: k_{OH} = 8.16 ± 0.01 $M^{-1}s^{-1}$ and k_0 = 6.63 ± 0.02 · 10^{-7} s^{-1} (**Fig. 2**)

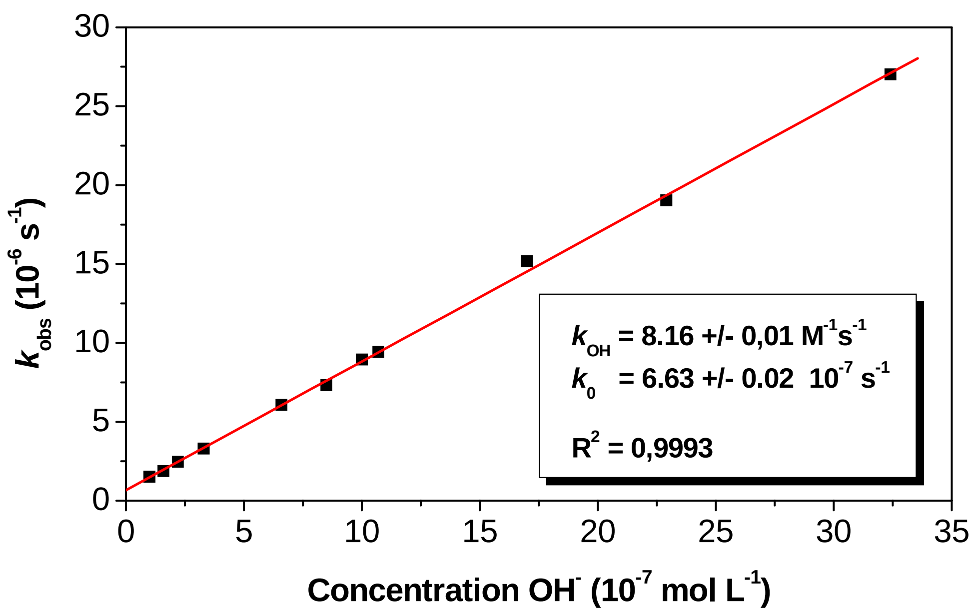


Fig. 2: k'_{obs} versus [OH^-] in the pH range 7.0 - 8.5.

A variation of the ionic strength in the range 0 to 50 mM at two different pH values did not lead to any significant change in the value of k'_{obs}.

A comparison between the experimentally determined values and the values from literature (**Table 9**) shows the influence of the buffer system and of the added co-solvent on the rate constants.

k_{OH} (M^{-1} s^{-1})	k_0 (s^{-1})	reaction conditions	literature
9.5	$< 1.66 \cdot 10^{-3}$	T = 25 °C, I = 1.0 M (KCl), 50 mM H_2O/triethylamine buffer	3a
23.5	---	T = 30 °C, I = 1.0 M (KCl), H_2O/Dioxan (1 %), pH control by 1 M KOH	3b
8.1	$7.28 \cdot 10^{-5}$	T = 25 °C, I = 0, H_2O/EtOH (28.5 %), phosphate buffer	3c
---	$4.3 \cdot 10^{-7}$	T = 25 °C, I = 1.0 M (KCl), H_2O, no buffer	3d
4.4; 8.1; 14.7	---	T = 15, 25, 35 °C, I = 0.1 M ($NaNO_3$), 20 mM CHES buffer, H_2O/CH_3CN (10 %)	3e
7.84	$1.12 \cdot 10^{-5}$	T = 25 °C, I = 0.1 M (KNO_3), 20 mM Tris buffer, H_2O/CH_3CN (10 %)	4a
19.41[a]	$8.16 \cdot 10^{-7}$	T = 25 °C, I = 0.1 M (KNO_3), 20 mM Tris buffer, H_2O/CH_3CN (10 %)	4b
12.41	$3.67 \cdot 10^{-6}$	T = 25 °C, I = 0.1 M (KNO_3), 20 mM „*Goods*“-buffer, H_2O/CH_3CN (10 %)	4c
14.8	---	T = 25 °C, I = 0.3 M (NaCl or KCl), 10 mM H_2O/triethylamin buffer	4d

[a] the k_{OH}-value is clearly very different from the other values. The authors have used for their calculations an unusual high value for ε_{NP} (20000 mol^{-1} L cm^{-1}, 400 nm) which probably leads to this discrepancy.

Table 9: Literature values for k_{OH} and k_0 in the spontaneous hydrolysis of NA.

The spontaneous hydrolysis of NA is generally one order of magnitude faster than any metal catalysed hydrolysis known at present. Therefore the rate of spontaneous hydrolysis of NA has to be determined experimentally for the reaction conditions employed.

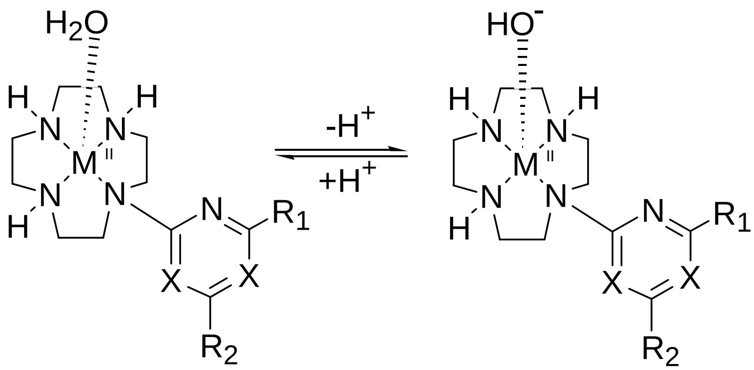
[3] a) J. F. Kirsch, W. P. Jencks, *J. Am. Chem. Soc.* **1964**, *86*, 837-846; b) T. C. Bruice, M. F. Mayahi; *J. Am. Chem. Soc.* **1960**, *82*, 3067 – 3071; c) T. C. Bruice, C. L. Schmir, *J. Am. Chem. Soc.* **1957**, *79*, 1663-1667; d) W. P. Jencks, M. Gilchrist, *J. Am. Chem. Soc*. **1968**, *90*, 2622-2637; e) T. Koike, M. Takamaru, E. Kimura; *J. Am. Chem. Soc.* **1994**, *116*, 8443 – 8449.

[4] a) S. Zhu, W. Chen, H.-K. Lin, X. Yin, F. Kou, M. Lin, Y. Chen; *Polyhedron* **1997**, *16*, 3285 – 3291; b) X.-C. Su, H.-W. Sun, Z.-F. Zhou, H.-K. Lin, L. Chen, S. Zhu, Y.-T. Chen; *Polyhedron* **2001**, *20*, 91 – 95; c) Y.-H. Guo, Q.-C. Ge, H. Lin, H.-K. Lin, S.-R. Zhu; *Int. J. Chem. Kinet.* **2004**, *36*, 41 – 48; d) W. P. Jencks, J.Carrioulo *J. Am. Chem. Soc*. **1960**, *82*, 1778-1786.

4. pH Profiles and species distribution diagrams of the metal complexes in aqueous solutions under nitrogen at 25 °C and I = 0.10 (TEAP).

In all graphs every second point is represented.

4.1. Mononuclear complexes



ZnL1 M = Zn^{II}, X = N, R_1 = R_2 = OMe

NiL1 M = Ni^{II}, X = N, R_1 = R_2 = OMe

ZnL3 M = Zn^{II}, X = N, R_1 = OMe, R_2 = 1-Aza-18-Crown-6

ZnL8 M = Zn^{II}, X = CH, R_1 = R_2 = H

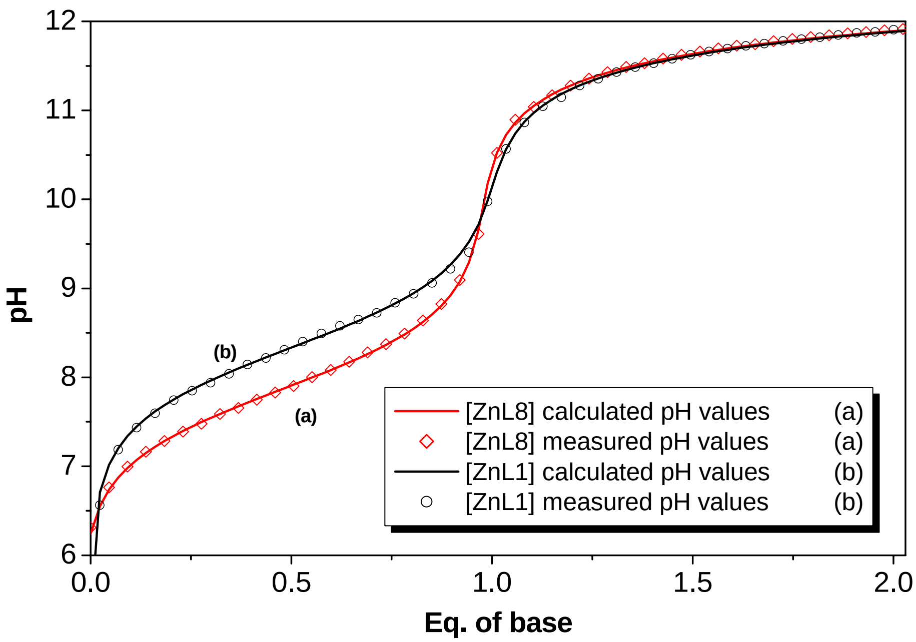


Figure 3. Titration curve for the complexes **[ZnL1](ClO_4)$_2$ · H_2O** and **[ZnL8](ClO_4)$_2$** in aqueous solution. The pH profile of **[ZnL3](ClO_4)$_2$** in aqueous solution is similar to that of **[ZnL1](ClO_4)$_2$ · H_2O** and was omitted for clarity reasons.

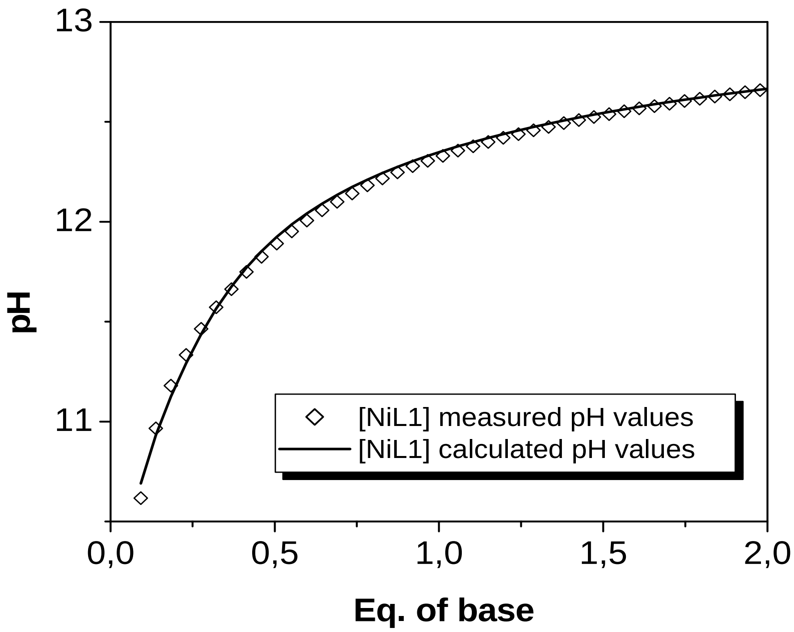


Figure 4. Titration curve for the complex **[NiL1](ClO_4)$_2$ · 2 H_2O** in aqueous solution

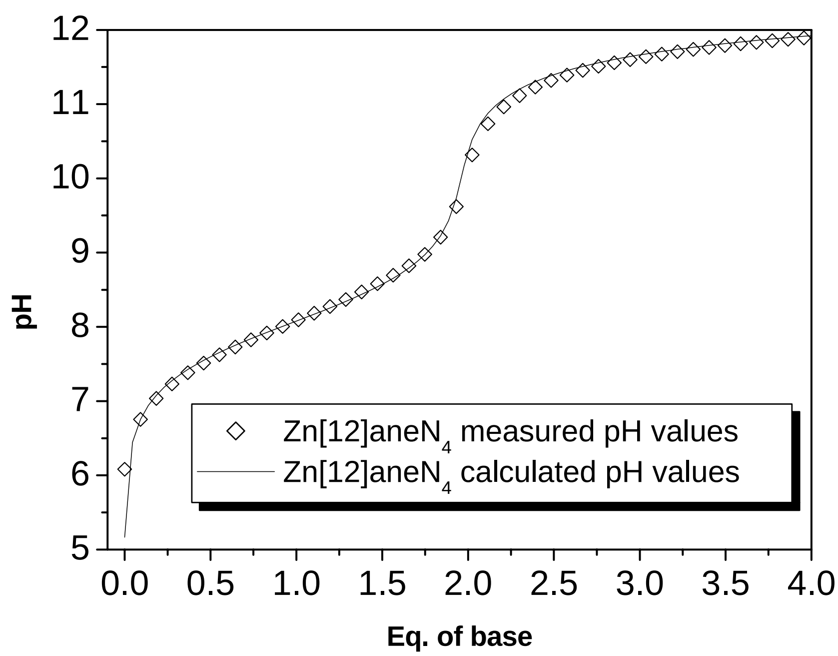


Figure 5. Titration curve for the complex **Zn[12]aneN$_4$ (ClO_4)$_2$**

With the help of the computer programme *Hyperquad* a distribution diagram of the de- and protonated species of the metal complexes over the whole pH range was obtained (**Figure 6**).

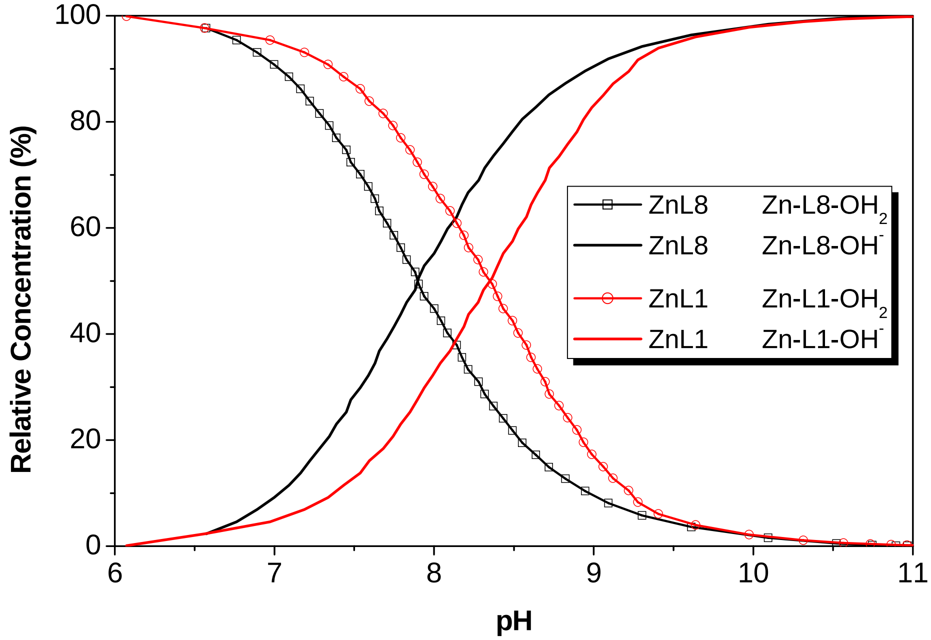


Figure 6. Species distribution diagram of the complexes **ZnL1** and **ZnL8**.

The profile of complex **ZnL3** is similar to that of **ZnL1** and was omitted for clarity reasons.

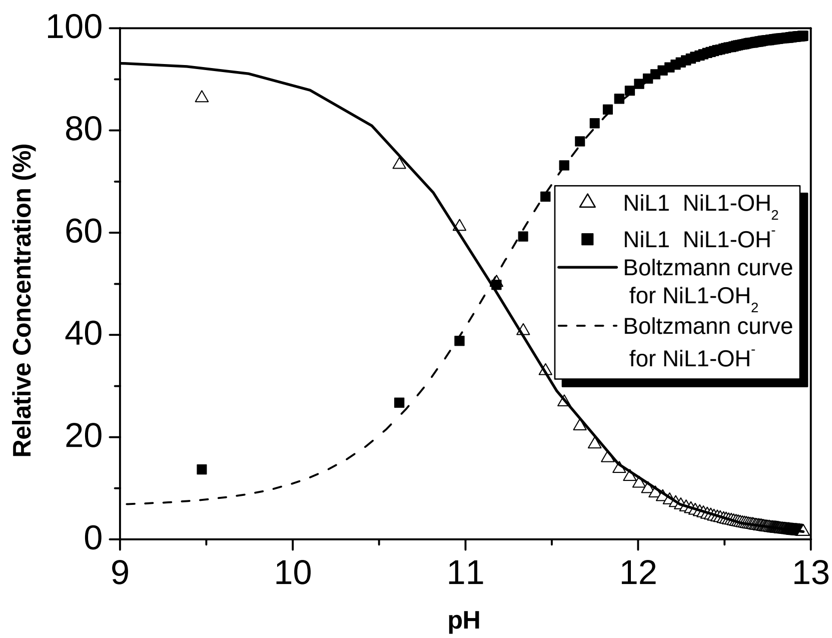


Figure 7. Species distribution diagram of the complex **NiL1**

4.2. Dinuclear complexes

4.2.1. pH titration curves

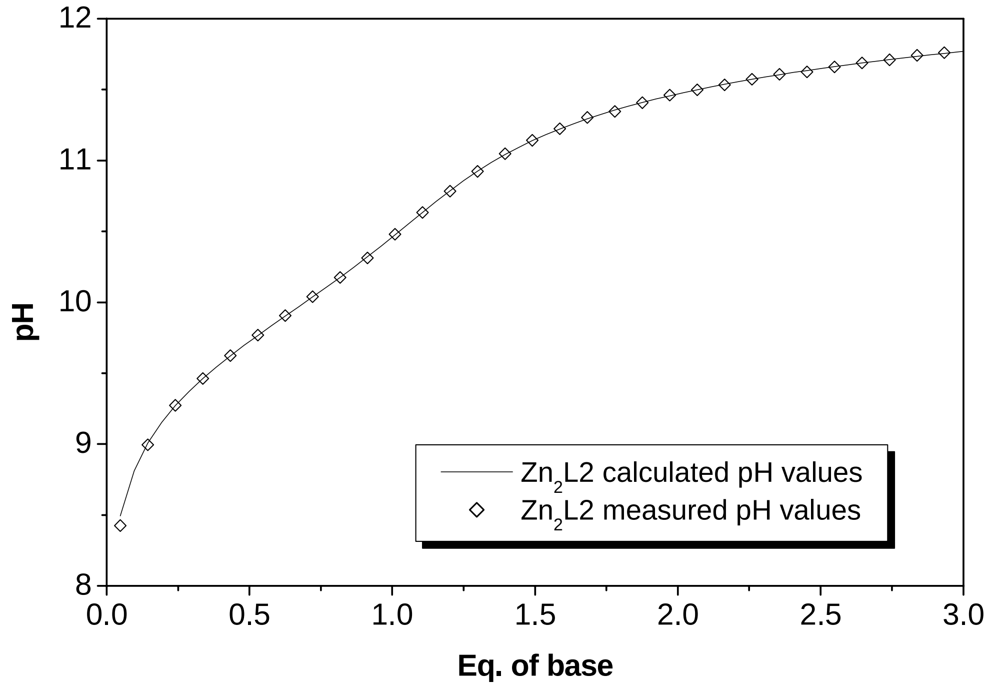


Figure 8. Titration curve for the complex **$[Zn_2L2](ClO_4)_4 \cdot CH_3CN$** in aqueous solution

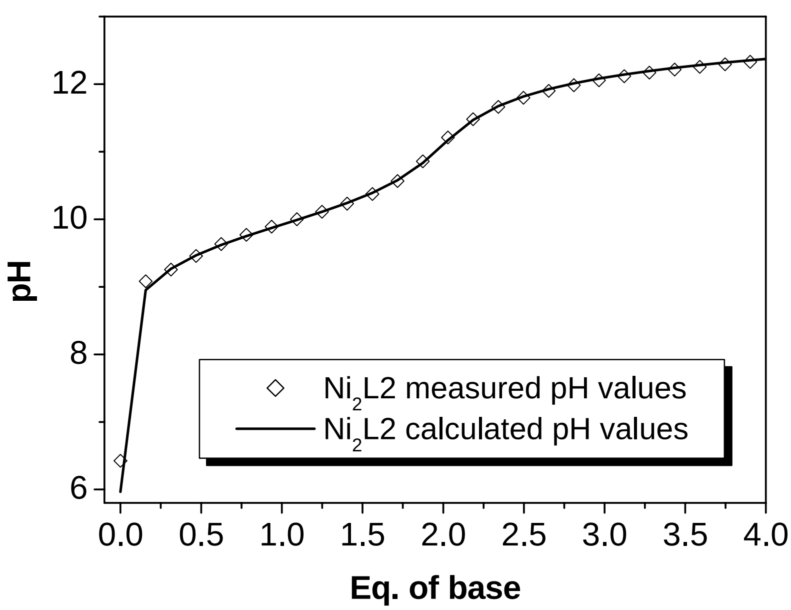


Figure 9. Titration curve for the complex **$[Ni_2L2](ClO_4)_4$** in aqueous solution

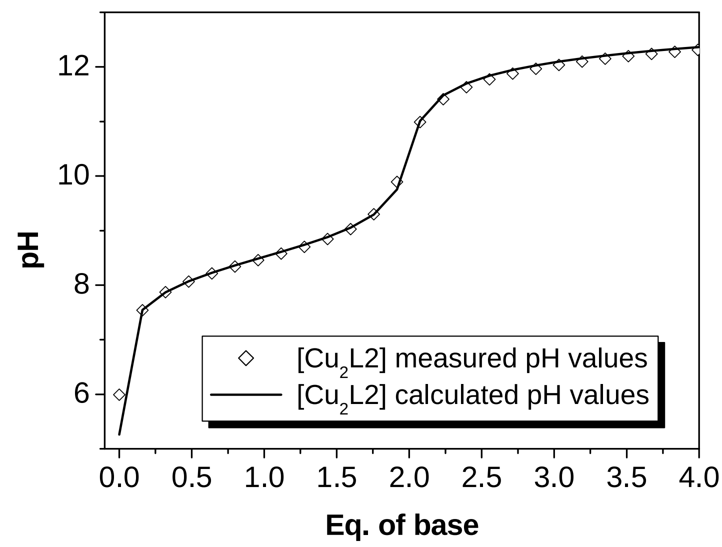


Figure 10. Titration curve for the complex **[Cu_2L2](ClO_4)$_4$ · 2 H_2O** in aqueous solution

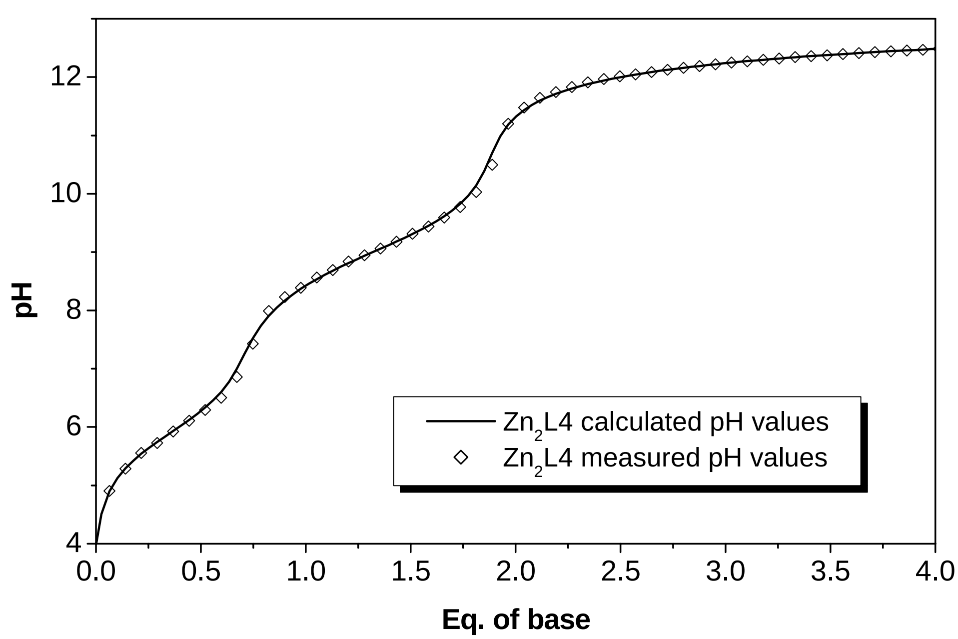


Figure 11. Titration curve for the complex **[Zn_2L4](ClO_4)$_4$** in aqueous solution (0.5 eq. $HClO_4$)

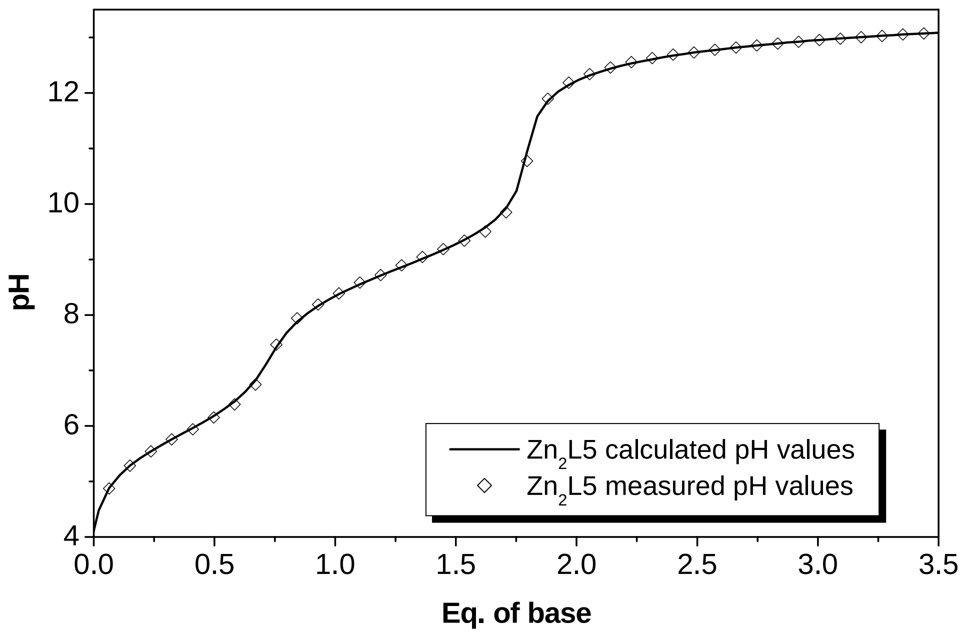


Figure 12. Titration curve for the complex **[Zn_2L5](ClO_4)$_4$ · H_2O** in MeOH/H_2O (9:1) solution (0.5 eq. $HClO_4$)

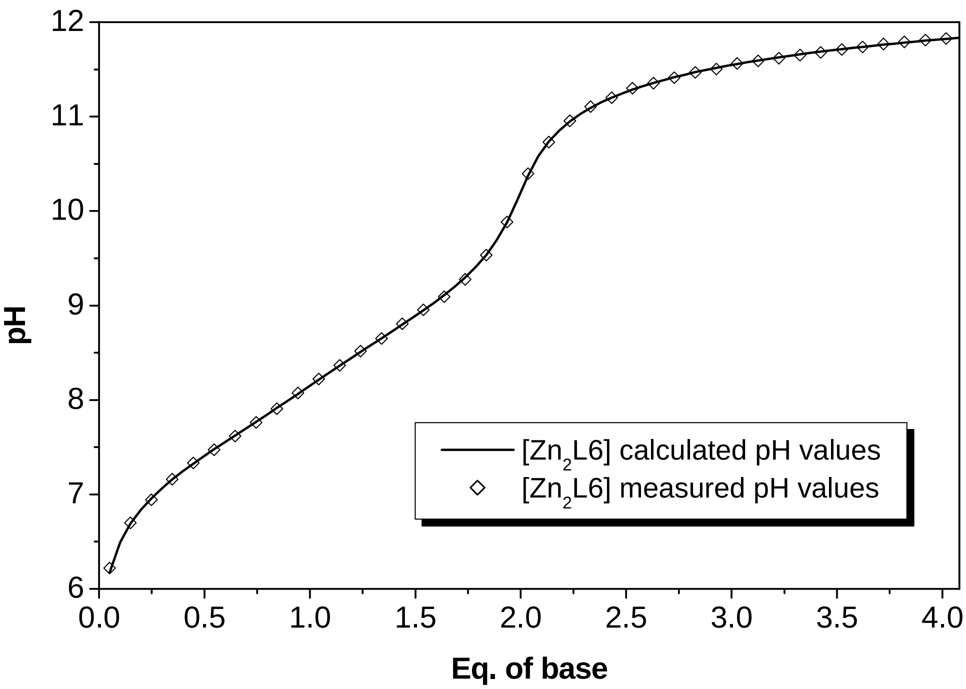


Figure 13. Titration curve for the complex **[Zn_2L6](ClO_4)$_4$ · H_2O** in aqueous solution.

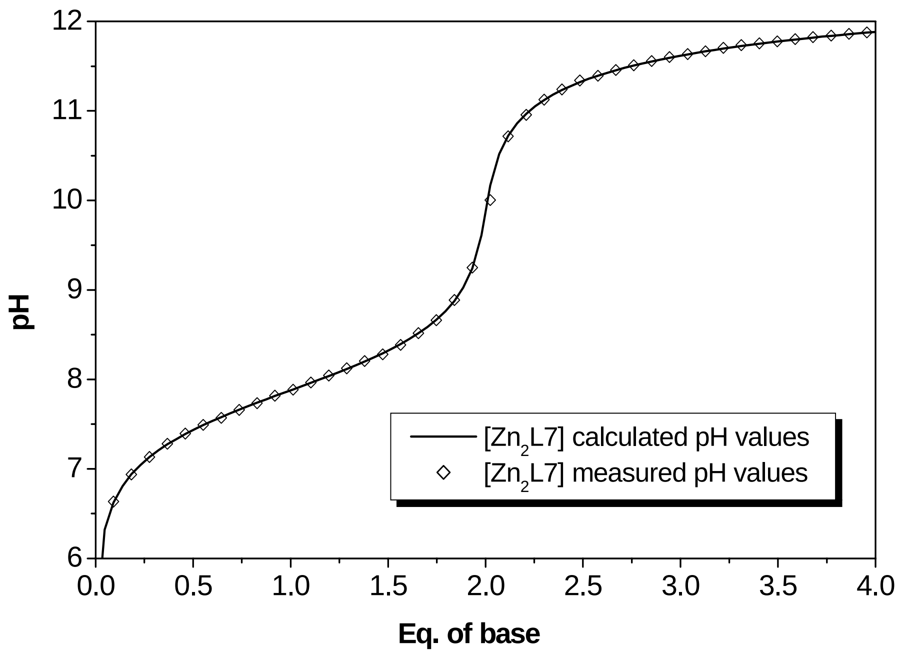


Figure 14. Titration curve for the complex **$[Zn_2L7](ClO_4)_4 \cdot CH_3CN$** in aqueous solution.

4.2.2. Species distribution diagrams

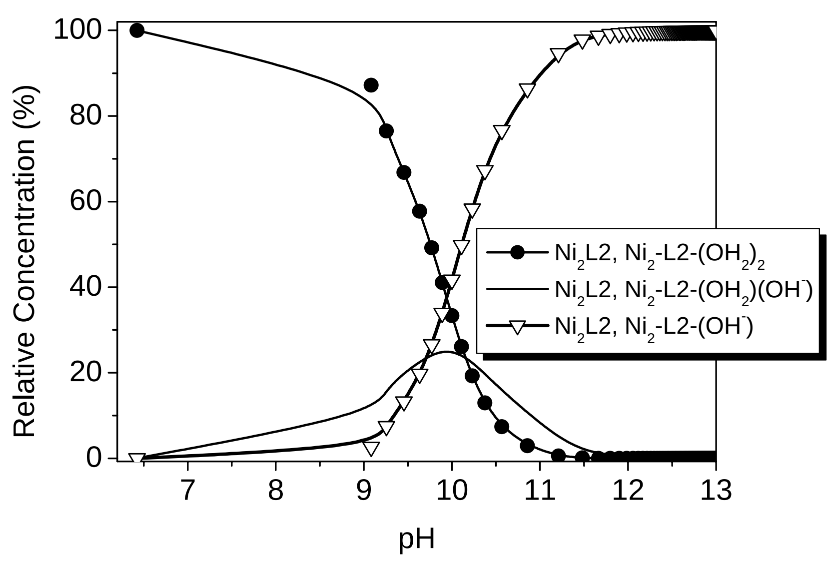


Figure 15. Species distribution diagram for **$[Ni_2L2](ClO_4)_4$** in aqueous solution.

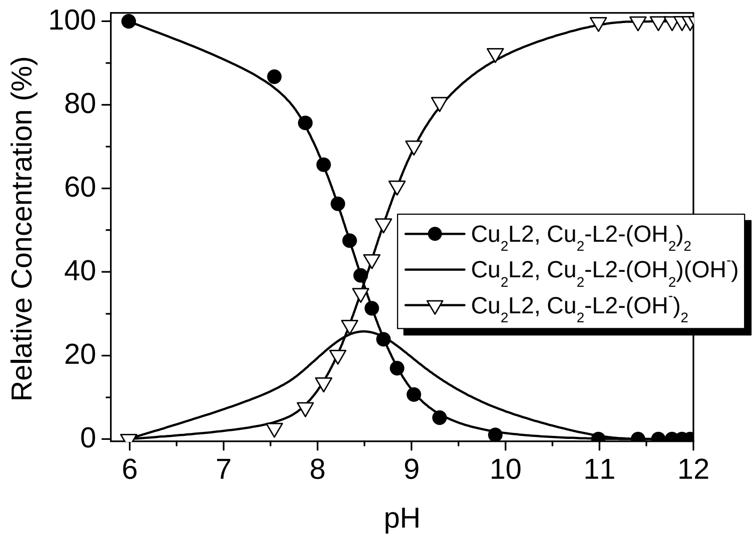


Figure 16. Species distribution diagram for **$[Cu_2L2](ClO_4)_4 \cdot 2H_2O$** in aqueous solution.

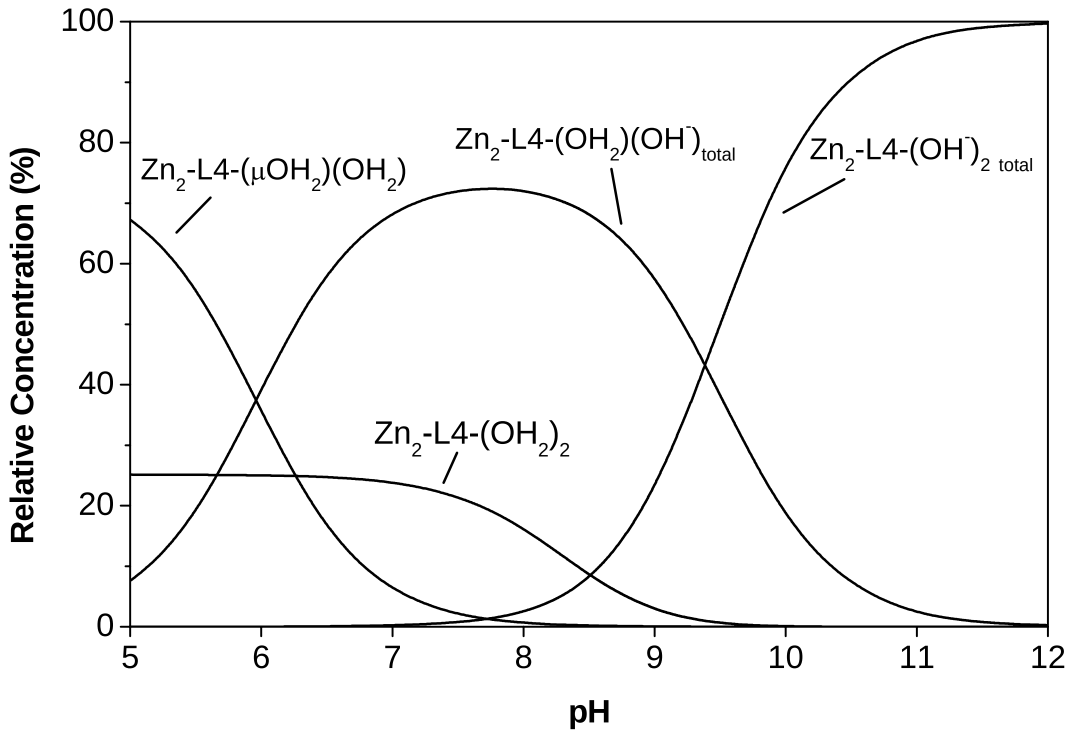


Figure 17. Species distribution diagram for **$[Zn_2L4](ClO_4)_4$** in aqueous solution.

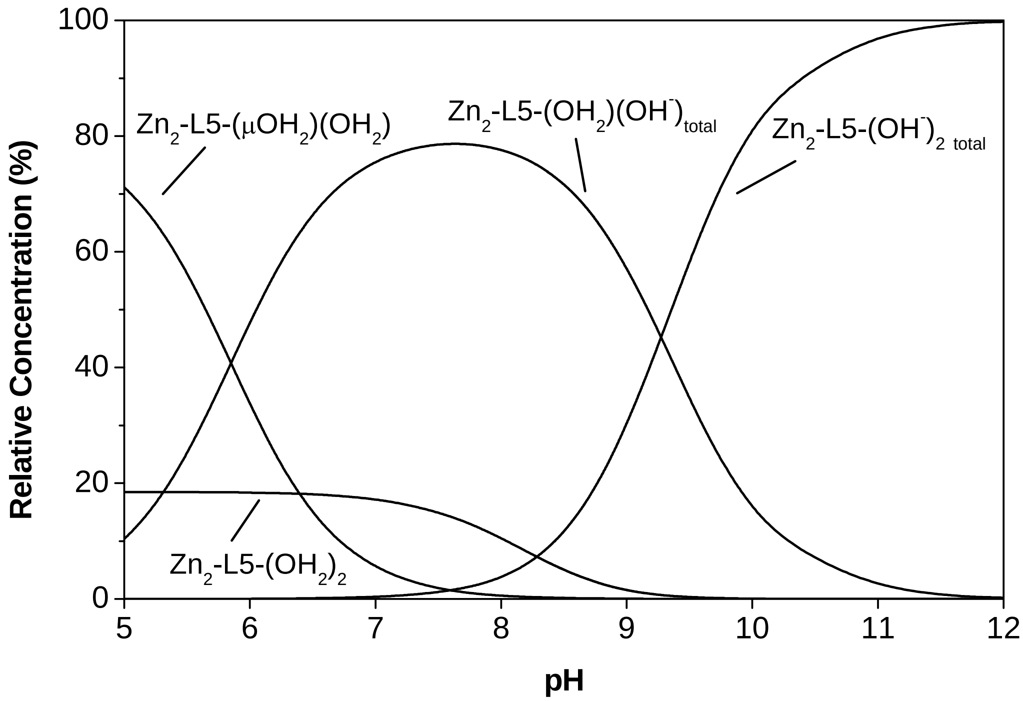


Figure 18. Species distribution diagram for **[Zn$_2$L5](ClO$_4$)$_4$ · H$_2$O** in MeOH/H$_2$O 9:1.

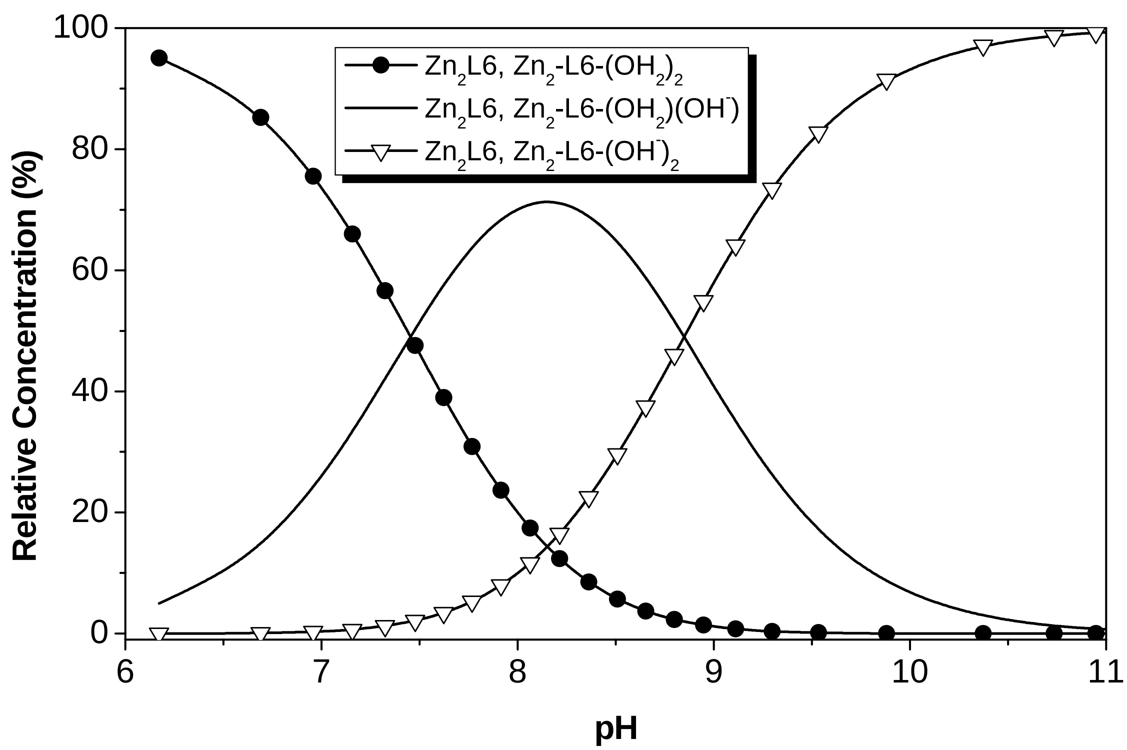


Figure 19. Species distribution diagram for **[Zn$_2$L6](ClO$_4$)$_4$ · H$_2$O** in aqueous solution.

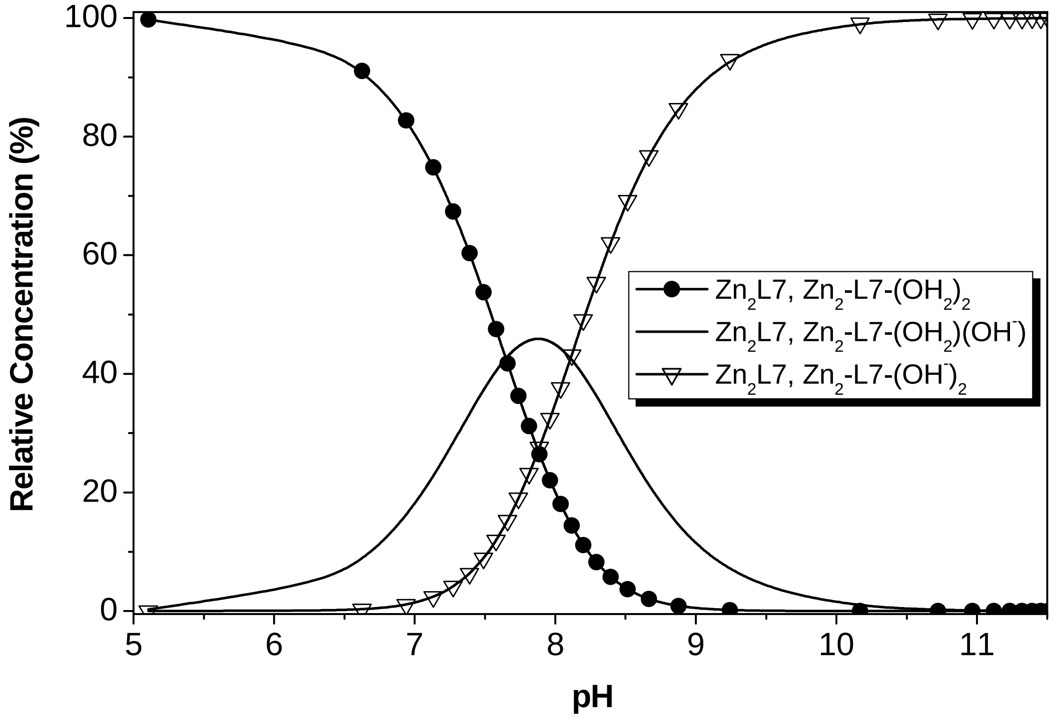


Figure 20. Species distribution diagram for **$[Zn_2L7](ClO_4)_4 \cdot CH_3CN$** in aqueous solution.

5. Plots of k_{obs} vs Zn(II) complex concentration and obtained k_{cat} values

5.1. Mononuclear Zn(II) complexes

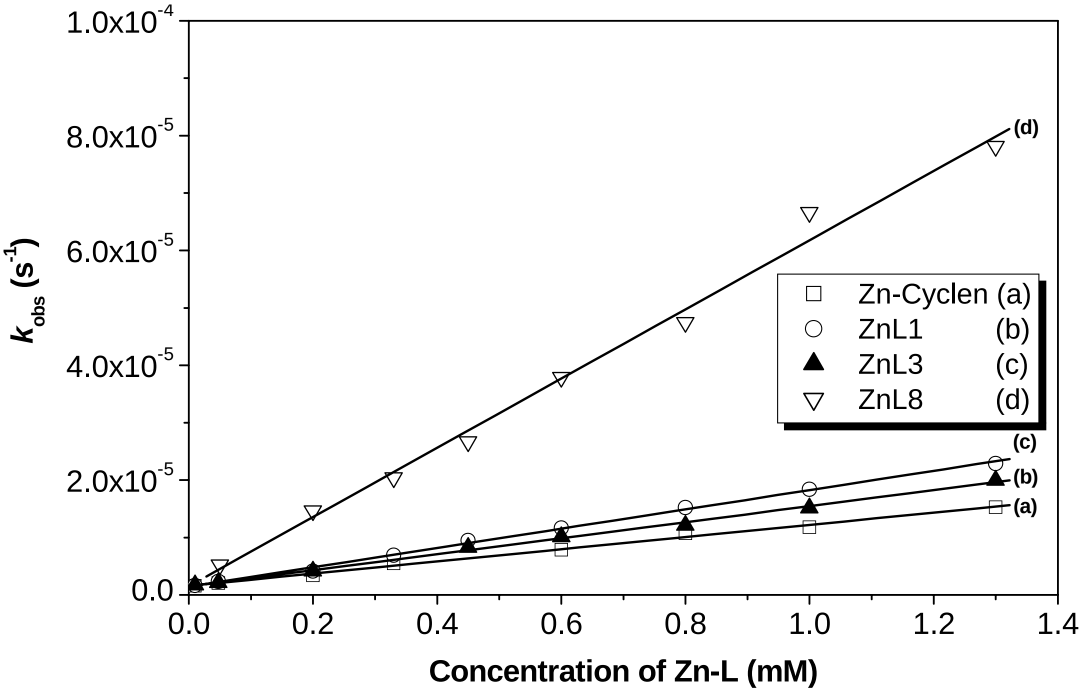


Figure 21: Calculation of the k_{cat} values for the mononuclear complexes at pH 7.

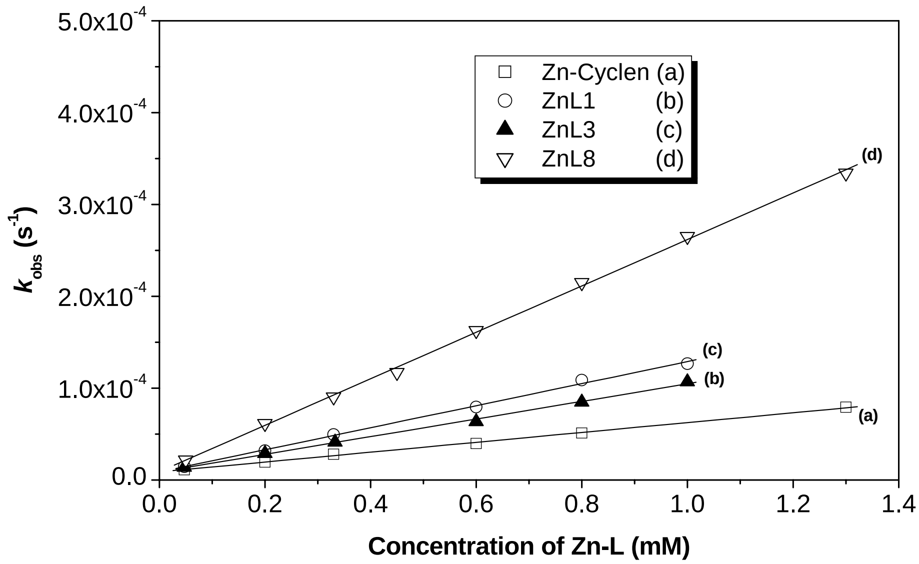


Figure 22: Calculation of the k_{cat} values for the mononuclear complexes at pH 8.

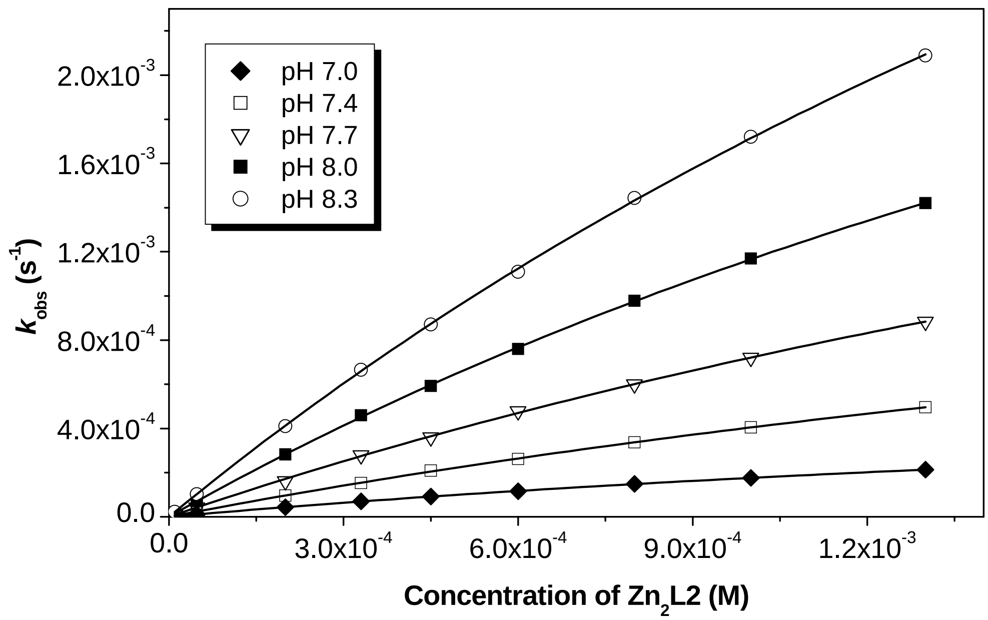
The value of k_{OH}, the second-order rate constant describes the nucleophilic attack of the OH^- ions and is derived from the intercepts of these plots. The obtained values for k_{OH} of 8.5 $M^{-1}s^{-1}$ for pH 7 and 8.23 $M^{-1}s^{-1}$ for pH 8 match the experimentally determined value of 8.16 $M^{-1}s^{-1}$. The minor deviation for pH 7 (maximum 11%) is due to the value of k_0, the first-order constant describing the solvolysis of the ester due to solvent molecules, which at this pH value is in the same order of magnitude as k_{OH}.

pH	**ZnL8** $10^2\ k_{cat}$ ($M^{-1}s^{-1}$)	**ZnL3** $10^2\ k_{cat}$ ($M^{-1}s^{-1}$)
6.71[a]	3.4	0.52
7.00[b]	6.0	1.4
7.43[b]	13.6	3.2
7.82[b]	21.5	7.4
8.00[b]	25.3	9.6
8.52[b]	33.5	17.0
8.99[b, c]	36.2	23.9
9.53[c]	38.1	26.1

[a] 50 mM HEPES buffer, 10% CH_3CN, I = 0.1 M (NaCl). [b] 50mM TRIS/HCl buffer, 10% CH_3CN, I = 0.1 M (NaCl). [c] CHES buffer [50mM], 10% CH_3CN, I = 0.1 M (NaCl). [d] Δ pH = ± 0.005, Δk_{cat} = ± 0.02 - 0.2 $\cdot 10^{-2}\ M^{-1}s^{-1}$

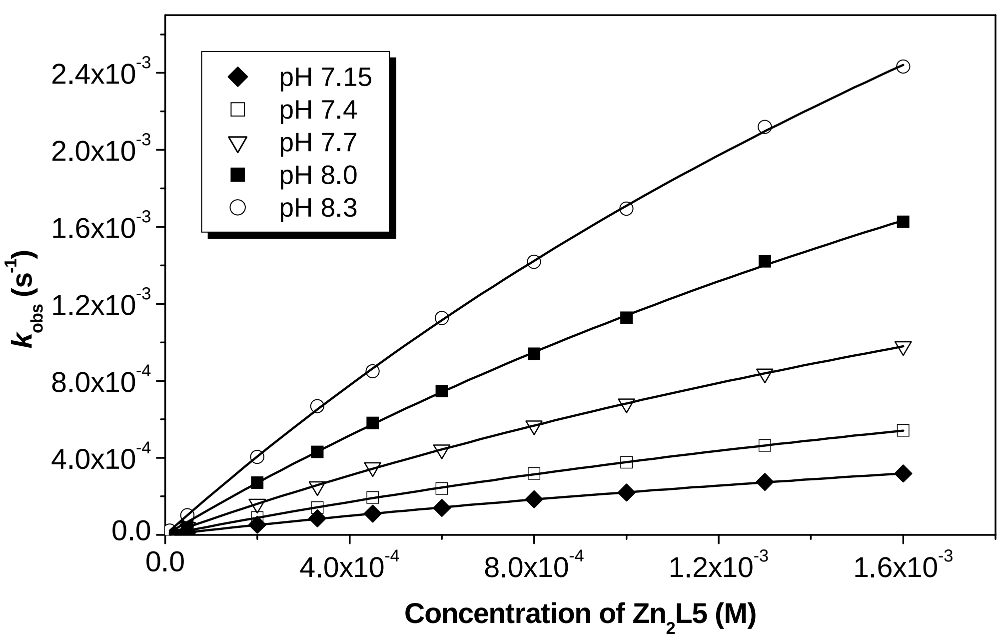
Table 10: Hydrolysis rate constants k_{cat} ($M^{-1}s^{-1}$) of **ZnL3** and **ZnL8** for the pH range 6.5 to 9.6 at 25 °C[d]

5.2. Dinuclear Zn(II) complexes



[a] 50 mM TRIS/HCl buffer, 10% CH_3CN, I = 0.1 M (NaCl), 25 °C, [NA] = 1.0 - 4.0 $\cdot 10^{-5}$ mol/L, Δ pH = ± 0.01, Δk_{obs} ± 0.4 - 2.7 %

Figure 23: Saturation kinetics for **Zn_2L2**[a]



[a] 50 mM TRIS/HCl buffer, 10% CH_3CN, I = 0.1 M (NaCl), 25 °C, [NA] = 1.0 - 4.0 $\cdot 10^{-5}$ mol/L, Δ pH = ± 0.01, Δk_{obs} ± 0.3 - 3.1 %

Figure 24: Saturation kinetics for **Zn_2L5**[a]

The saturation kinetics for these complexes is less obvious due to their lower solubility in aqueous solutions.

6. Results obtained from the saturation kinetic curves of Zn_2L2, Zn_2L4 and Zn_2L5.

Complex	pH	10^3 k'_{cat} (s^{-1})[a]	10^3 K_M (M)[b]	k'_{cat}/K_M ($M^{-1}s^{-1}$)[c]
Zn_2L4	7.0	0.81 ± 0.20	4.3 ± 0.13	0.19
	7.4	1.9 ± 0.06	4.5 ± 0.19	0.42
	7.7	3.3 ± 0.12	4.4 ± 0.24	0.73
	8.0	5.3 ± 0.13	4.4 ± 0.15	1.22
	8.3	7.4 ± 0.21	4.1 ± 0.17	1.80
Zn_2L2	7.0	0.84 ± 0.41	3.8 ± 0.21	0.22
	7.4	2.0 ± 0.07	3.9 ± 0.18	0.51
	7.7	3.6 ± 0.20	4.0 ± 0.28	0.90
	8.0	5.5 ± 0.11	3.8 ± 0.12	1.48
	8.3	8.3 ± 0.25	3.8 ± 0.14	2.17
Zn_2L5	7.15	1.2 ± 0.06	4.5 ± 0.27	0.27
	7.4	2.0 ± 0.08	4.2 ± 0.21	0.47
	7.7	3.6 ± 0.10	4.2 ± 0.15	0.85
	8.0	5.8 ± 0.26	4.1 ± 0.23	1.42
	8.3	8.5 ± 0.35	4.0 ± 0.21	2.14

[a] $\Delta k'_{cat} = \pm 2.4 - 4.9$ %.[b] $\Delta K_M = \pm 3.1 - 6.9$ %.[c] $k'_{cat}/K_M = k_{cat}$ (bimolecular), $\Delta k_{cat} = \pm 3.9 - 8.2$ %. [d] The regression coefficients $R^2 > 0.9997$ were obtained.

Table 11: Results obtained from the non-linear fit of equation **(6)**[d].

The higher error margins compared to the mononuclear Zn(II) complexes are due to the non-linear fit, which requires an extrapolation over a higher concentration range.

7. Second-order rate constants $k_{cat\ 1,2}$ ($M^{-1}s^{-1}$) for Zn_2L7 and Zn_2L6.

pH	$k_{cat\ 1,2}$ ($M^{-1}s^{-1}$)	pH	$k_{cat\ 1,2}$ ($M^{-1}s^{-1}$)	pH	$k_{cat\ 1,2}$ ($M^{-1}s^{-1}$)
6.22[a]	0.0149	7.38[c]	0.1813	8.76[c]	0.7019
6.54[a]	0.0312	7.59[c]	0.2671	8.76[d]	0.7053
6.72[a]	0.0461	7.71[c]	0.3221	9.00[c]	0.7340
6.72[b]	0.0456	7.81[c]	0.3788	9.15[d]	0.7516
6.83[b]	0.0551	8.00[c]	0.4481	9.34[d]	0.7701
6.92[b]	0.0724	8.12[c]	0.5048	9.57[d]	0.7786
7.11[b]	0.1100	8.20[c]	0.5404	9.79[d]	0.7832
7.11[c]	0.1087	8.34[c]	0.6022	9.99[d]	0.7867
7.31[c]	0.1559	8.52[c]	0.6453	10.18[d]	0.7866

[a] BIS/TRIS buffer [50 mM], 10 % CH_3CN, I = 0.1 M (NaCl), 25 °C. [b] HEPES buffer [50 mM], 10% CH_3CN, I = 0.1 M (NaCl), 25 °C. [c] TRIS/HCl buffer [50 mM], 10% CH_3CN, I = 0.1 M (NaCl), 25 °C. [d] CHES buffer [50 mM], 10% CH_3CN, I = 0.1 M (NaCl), 25 °C.

Δ pH = ± 0.005, $\Delta k_{cat\ 1,2}$ = ± 0.05 - 0.3 $\cdot 10^{-2}$ $M^{-1}s^{-1}$, $\Delta k_{obs\ 1,2}$ = ± 0.5 - 3.8%

Table 12: $k_{cat\ 1,2}$ values for **Zn_2L7** for the pH range 6.2 to 10.2.

pH	$k_{cat\ 1,2}$ ($M^{-1}s^{-1}$)	pH	$k_{cat\ 1,2}$ ($M^{-1}s^{-1}$)	pH	$k_{cat\ 1,2}$ ($M^{-1}s^{-1}$)
6.29[a, e]	0.0370	7.21[c]	0.2193	8.71[d]	0.6175
6.58[a, e]	0.0699	7.49[c]	0.3191	9.01[c]	0.6580
6.91[a, e]	0.1273	7.81[c]	0.4112	9.32[d]	0.6746
6.91[b, e]	0.1283	8.12[c]	0.4979	9.59[d]	0.6999
7.03[b, e]	0.1590	8.40[c]	0.5601	9.91[d]	0.7017
7.03[c, e]	0.1528	8.71[c]	0.6190	10.18[d]	0.7097

[a] BIS/TRIS buffer [50 mM], 10% CH_3CN, I = 0.1 M (NaCl), 25 °C. [b] HEPES buffer [50 mM], 10% CH_3CN, I = 0.1 M (NaCl), 25 °C. [c] TRIS/HCl buffer [50 mM], 10% CH_3CN, I = 0.1 M (NaCl), 25 °C. [d] CHES buffer [50 mM], 10% CH_3CN, I = 0.1 M (NaCl), 25 °C. [e] The $k_{cat\ 1,2}$ value corresponds to the $k_{cat\ 1}$ value, as the percentage of dihydroxy species present in solution is less than 0.5% for these pH values.

Δ pH = ± 0.005, $\Delta k_{cat\ 1,2}$ = ± 0.05 - 0.35 $\cdot 10^{-2}$ $M^{-1}s^{-1}$, $\Delta k_{obs\ 1,2}$ = ± 0.6 - 3.6%

Table 13: $k_{cat\ 1,2}$ values for **Zn_2L6** for the pH range 6.2 to 10.2.

8. Graphical representation of the relationship between measured $k_{cat\ 1,2}$, the species-distribution diagram and the calculated $k_{cat\ 1}$ and $k_{cat\ 2}$ for Zn_2L7 and Zn_2L6.

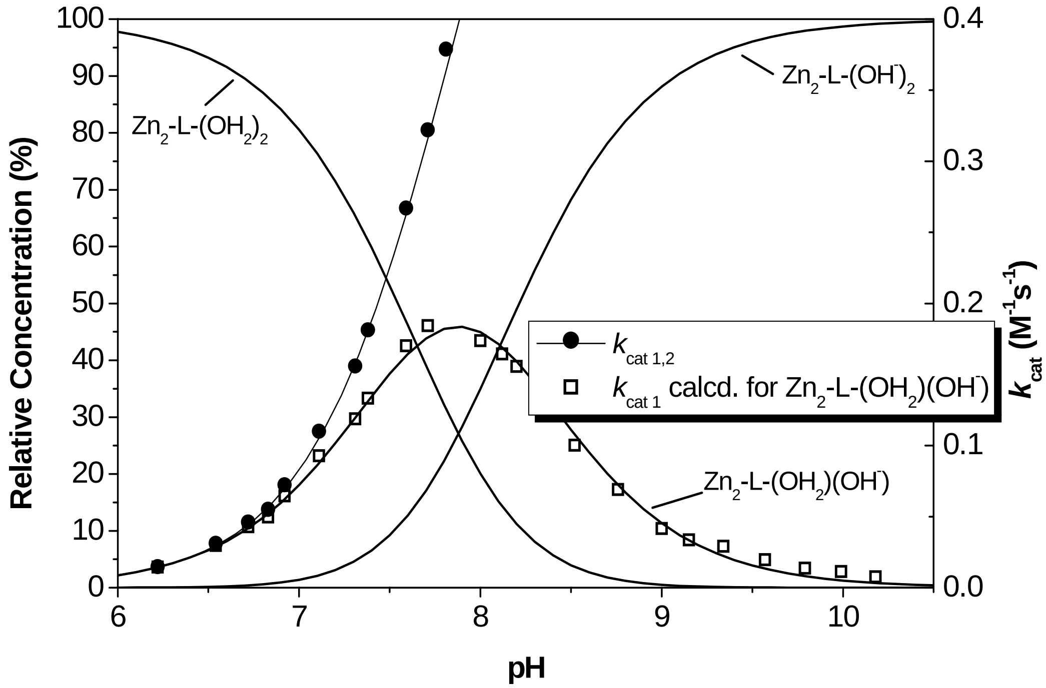


Figure 25: Species-distribution diagram of $\mathbf{Zn_2L7}$ with measured $k_{cat\ 1,2}$ values and calculated $k_{cat\ 1}$ values.

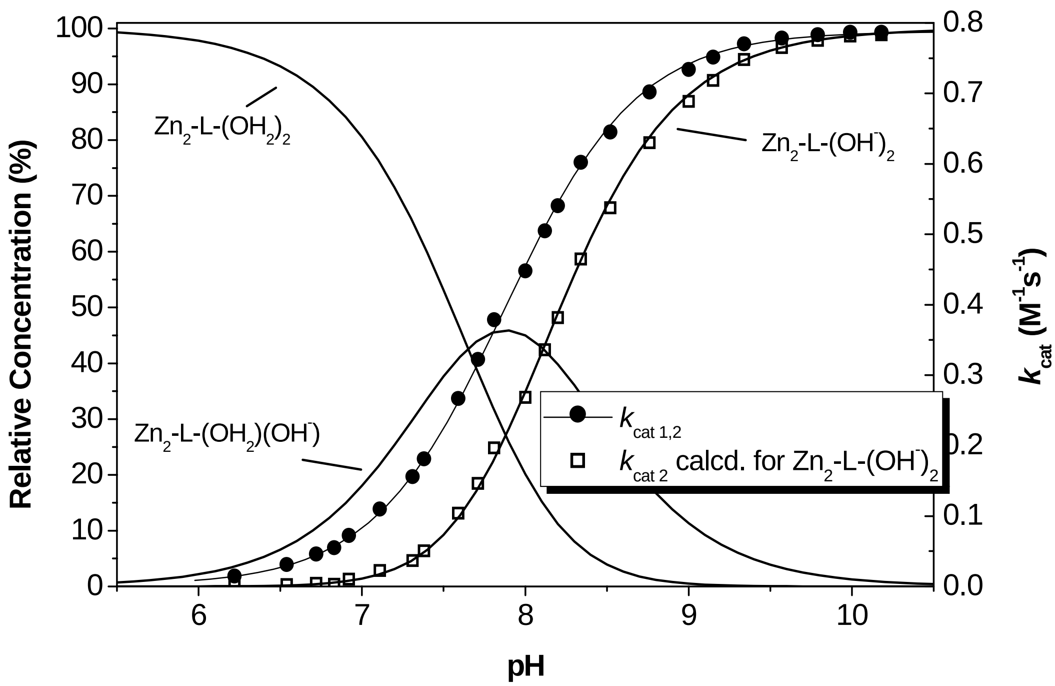


Figure 26: Species-distribution diagram of $\mathbf{Zn_2L7}$ with measured $k_{cat\ 1,2}$ values and calculated $k_{cat\ 2}$ values.

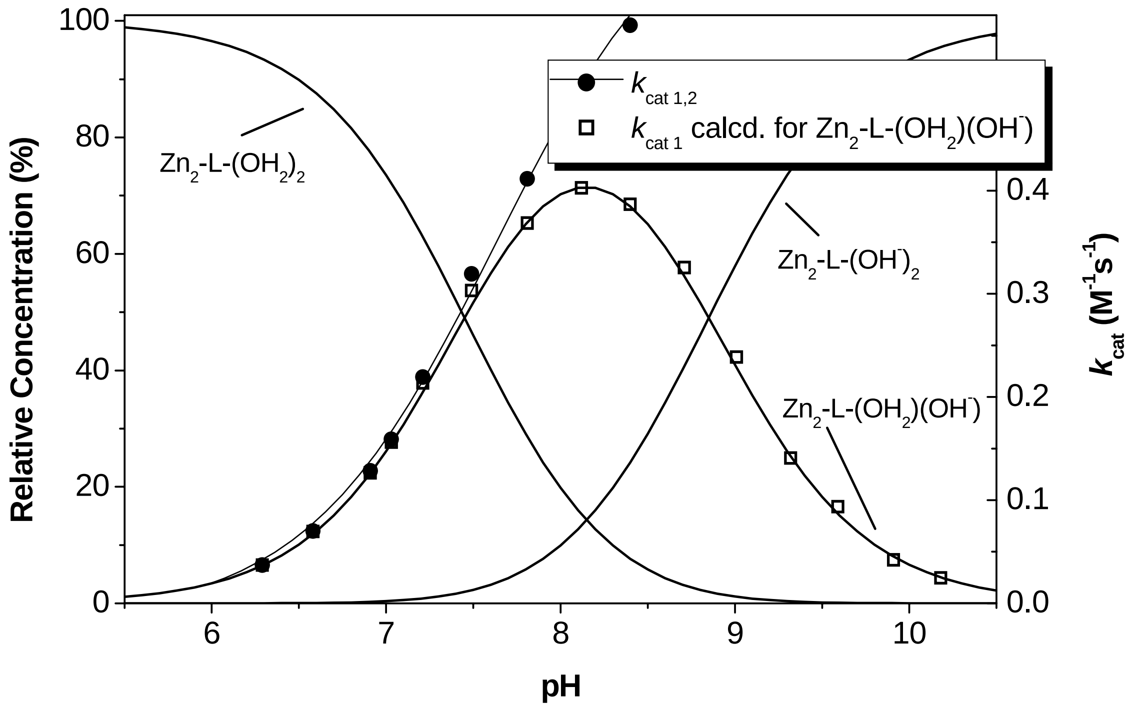


Figure 27: Species-distribution diagram of **Zn_2L6** with measured $k_{cat\ 1,2}$ values and calculated $k_{cat\ 1}$ values.

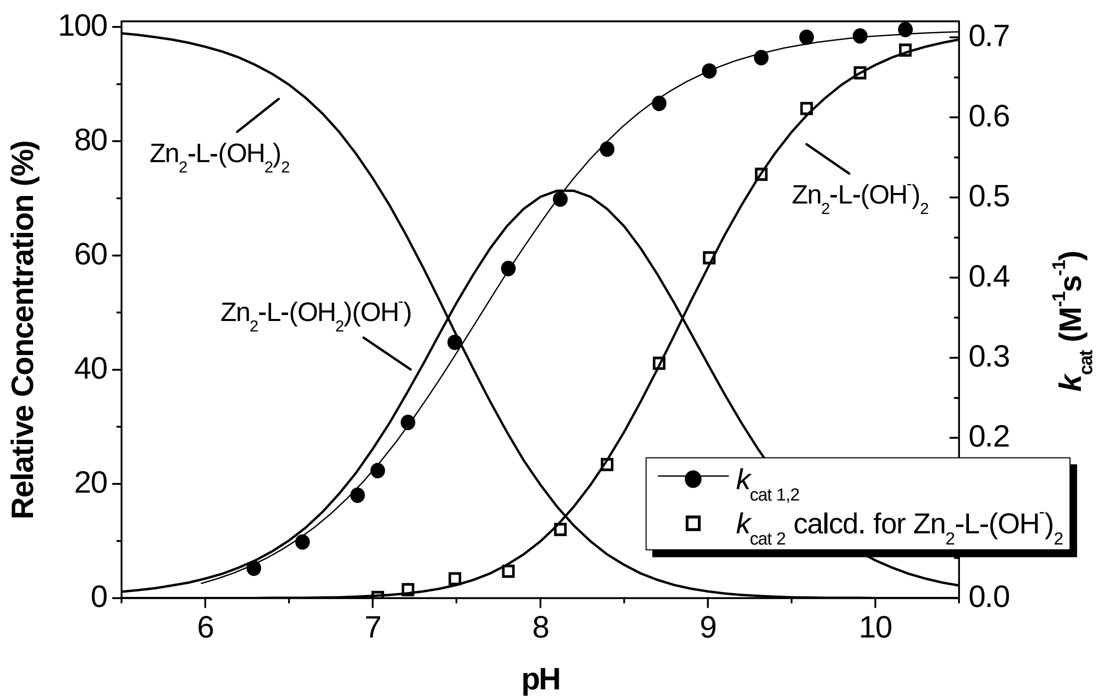


Figure 28: Species-distribution diagram of **Zn_2L6** with measured $k_{cat\ 1,2}$ values and calculated $k_{cat\ 2}$ values.