Eur. J. Inorg. Chem. **2007** · © WILEY-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2007 · ISSN 1434–1948

SUPPORTING INFORMATION

Title: Ternary Complexes of Zinc(II), Cyclen and Pyridinecarboxylic Acids
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Ref. No.: I200700183

Table S1 Selected bond lengths (Å) and angles (°) found in the studied crystal structures.

[Zn(cyclen)(NO$_3$)]ClO$_4$				[Zn(cyclen)(L^4)](ClO$_4$)$_2$			
bonds	Å	angles	°	bonds	Å	angles	°
Zn–O1	1.998(3)	O1-Zn-N11	116.31(16)	Zn–N1	2.029(3)	N1-Zn-N11	118.80(13)
Zn–N11	2.097(4)	O1-Zn-N14	106.97(17)	Zn–N11	2.112(3)	N1-Zn-N14	111.20(13)
Zn–N14	2.148(5)	O1-Zn-N17	109.46(16)	Zn–N14	2.139(4)	N1-Zn-N17	104.94(13)
Zn–N17	2.124(4)	O1-Zn-N110	113.95(17)	Zn–N17	2.136(3)	N1-Zn-N110	110.99(13)
Zn–N110	2.124(5)	N11-Zn-N14	82.2(2)	Zn–N110	2.164(3)	N11-Zn-N14	82.81(16)
N1–O1	1.255(5)	N11-Zn-N17	134.09(17)			N11-Zn-N17	136.25(14)
N1–O2	1.196(6)	N11-Zn-N110	83.0(2)			N11-Zn-N110	82.26(15)
N1–O3	1.213(5)	N14-Zn-N17	81.5(2)			N14-Zn-N17	82.34(16)
		N14-Zn-N110	138.92(19)			N14-Zn-N110	137.39(14)
		N17-Zn-N110	81.8(2)			N17-Zn-N110	81.47(15)

[{Zn(cyclen)}$_2$(μ$_2$-L^2)](ClO$_4$)$_3$				[{Zn(cyclen)}$_2$(μ$_2$-η^1:η^2-L^1)](ClO$_4$)$_3$·H$_2$O			
bonds	Å	bonds	Å	bonds	Å	bonds	Å
Zn1–N1	2.026(2)			Zn1–N1	2.154(9)		
		Zn2–O1	1.9237(18)	Zn1–O1	2.232(8)	Zn2–O2	1.945(8)
Zn1–N11	2.123(2)	Zn2–N21	2.137(2)	Zn1–N11	2.128(10)	Zn2–N21	2.079(16)
Zn1–N14	2.129(2)	Zn2–N24	2.133(3)	Zn1–N14	2.143(12)	Zn2–N24	2.157(18)
Zn1–N17	2.146(2)	Zn2–N27	2.168(3)	Zn1–N17	2.201(11)	Zn2–N27	2.110(15)
Zn1–N110	2.139(2)	Zn2–N210	2.111(2)	Zn1–N110	2.142(11)	Zn2–N210	2.127(17)
C3–C7	1.507(3)			C2–C7	1.488(15)		
C7–O1	1.273(3)			C7–O1	1.237(13)		
C7–O2	1.234(3)			C7–O2	1.257(13)		
angles	°	angles	°	angles	°	angles	°
				N1-Zn1-O1	74.9(3)		
		O1-Zn2-N21	116.93(9)	O1-Zn1-N11	83.1(3)	O2-Zn2-N21	123.7(5)
		O1-Zn2-N24	102.92(9)	O1-Zn1-N14	106.6(5)	O2-Zn2-N24	107.4(6)
		O1-Zn2-N27	105.84(9)	O1-Zn1-N17	171.1(4)	O2-Zn2-N27	101.1(6)
		O1-Zn2-N210	120.01(9)	O1-Zn1-N110	94.2(4)	O2-Zn2-N210	116.7(5)
N1-Zn1-N11	117.08(9)			N1-Zn1-N11	157.9(4)		
N1-Zn1-N14	114.90(9)			N1-Zn1-N14	102.2(5)		
N1-Zn1-N17	106.40(9)			N1-Zn1-N17	98.4(4)		
N1-Zn1-N110	107.64(9)			N1-Zn1-N110	102.0(4)		
N11-Zn1-N14	81.84(9)	N21-Zn2-N24	82.26(11)	N11-Zn1-N14	81.9(5)	N21-Zn2-N24	80.0(9)
N11-Zn1-N17	136.43(9)	N21-Zn2-N27	136.69(9)	N11-Zn1-N17	103.7(4)	N21-Zn2-N27	135.1(7)
N11-Zn1-N110	82.61(9)	N21-Zn2-N210	82.64(10)	N11-Zn1-N110	81.5(5)	N21-Zn2-N210	80.9(9)
N14-Zn1-N17	82.69(9)	N24-Zn2-N27	81.92(11)	N14-Zn1-N17	80.3(6)	N24-Zn2-N27	84.8(11)
N14-Zn1-N110	137.28(9)	N24-Zn2-N210	136.79(10)	N14-Zn1-N110	151.5(5)	N24-Zn2-N210	135.5(7)
N17-Zn1-N110	81.78(9)	N27-Zn2-N210	81.95(10)	N17-Zn1-N110	81.4(5)	N27-Zn2-N210	81.0(11)

Fig. S2 Arrangement of the chelate rings in [{Zn(cyclen)}$_2$(μ-η^1:η^2-L^1-*N,N,O'*)]$^{3+}$ cation found in the structure of [{Zn(cyclen)}$_2$(μ-η^1:η^2-L^1-*N,N,O'*)]$(ClO_4)_3$·H_2O.

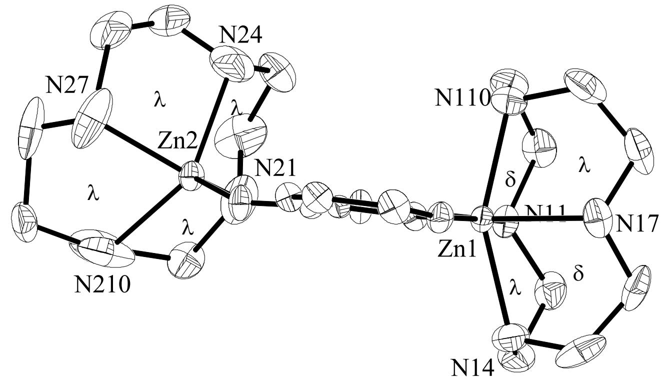

Fig. S3 Distribution of the complex species formed in the Zn^{2+}-H_xL^n systems as a function of $-\log[H^+]$; HL^1 = picolinic acid, HL^2 = nicotinic acid, H_2L^3 = dipicolinic acid, L^4 = nicotinamide, molar ratio Zn^{2+}-H_xL^n = 1:2, $c(Zn^{2+})$ = 0.004 mol dm^{-3}.

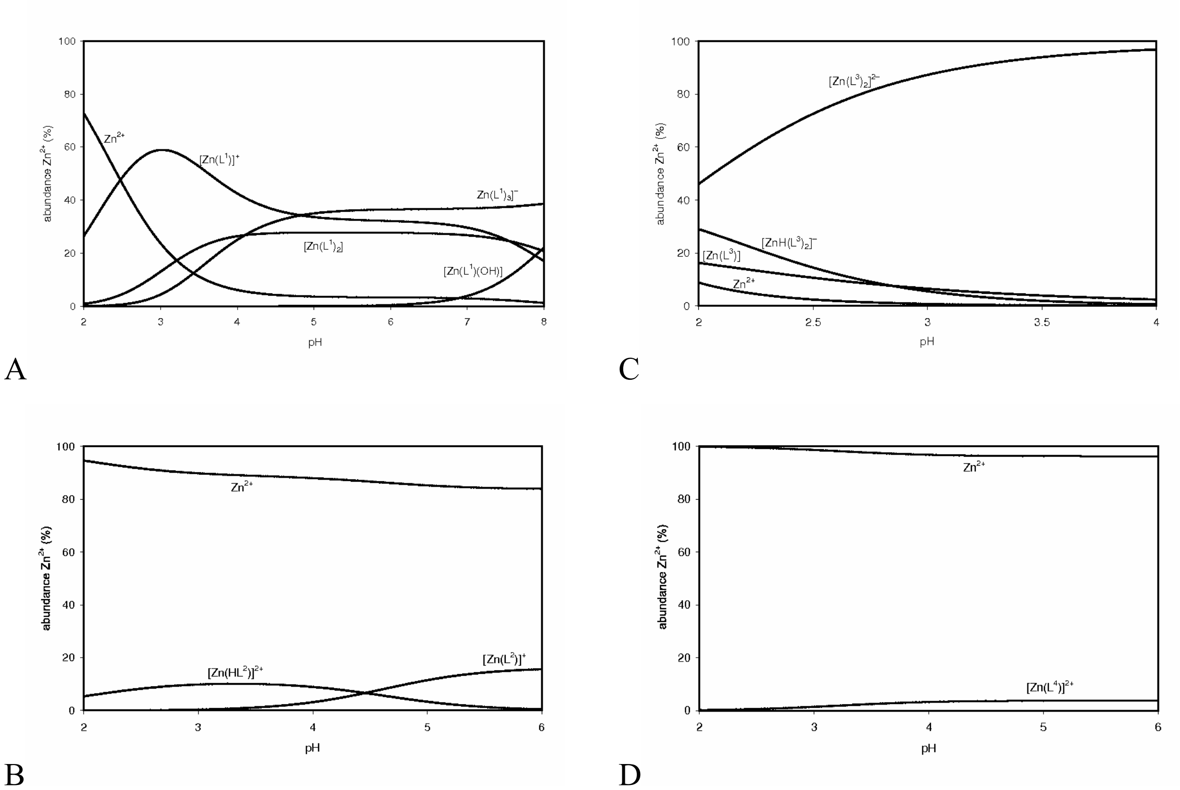

Fig. S4 Distribution of the complex species formed in the Zn^{2+}-cyclen system as a function of $-\log[H^+]$; $c(Zn^{2+}) = c(\text{cyclen}) = 0.004\ \text{mol dm}^{-3}$.

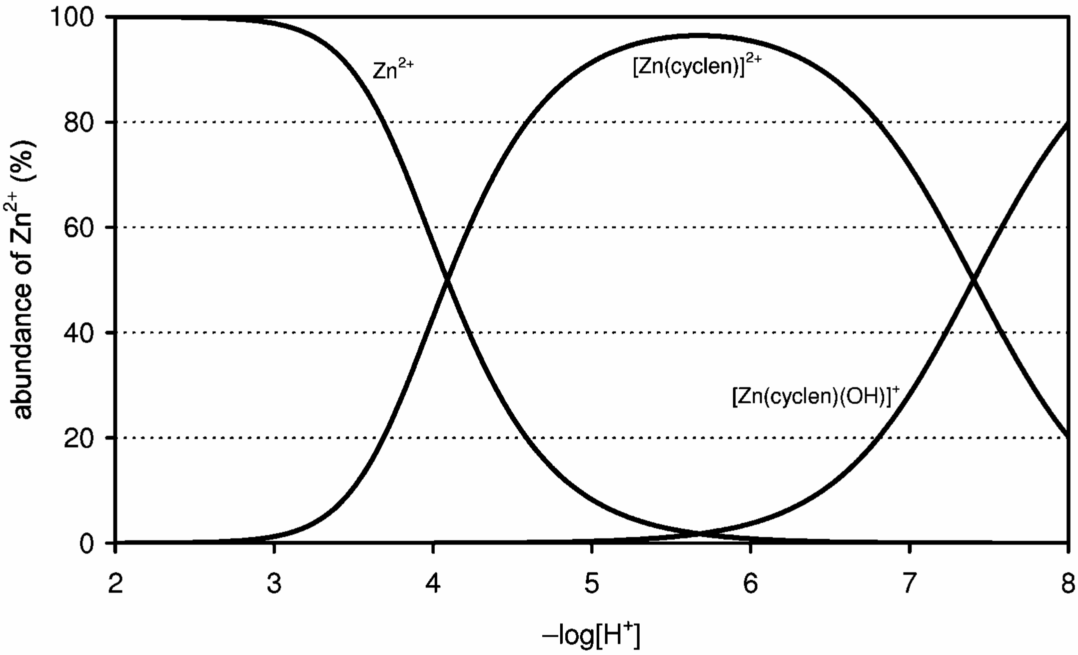

Fig. 5

Calculated distribution of Zn^{2+} in the ternary Zn^{2+}-cyclen-H_xL^n systems as a function of –log[H^+] for molar ratio Zn^{2+}:cyclen:H_xL^n = 1:1:1 – A) HL^1, B) HL^2, C) H_2L^3 (binary Zn^{2+}-cyclen species (green), binary Zn^{2+}-H_xL^n species (blue) and ternary Zn^{2+}-cyclen-H_xL^n species (red)). Comparison of total abundance of all binary Zn^{2+}-cyclen species in the ternary 1:1:1 mixtures (green), all binary Zn^{2+}-H_xL^n species in the ternary 1:1:1 mixtures (blue) and all ternary complexes (red) with total abundance of Zn^{2+}-cyclen (dotted red) and Zn^{2+}-H_xL^n (dotted blue) complexes found in the binary mixtures for Zn^{2+}:cyclen = 1:1 and Zn^{2+}:H_xL^n = 1:1, respectively – D) HL^1, E) HL^2, F) H_2L^3. Abbreviation "cyc" stays for cyclen, $c(Zn^{2+})$ = 0.004 mol dm^{-3} in all cases.

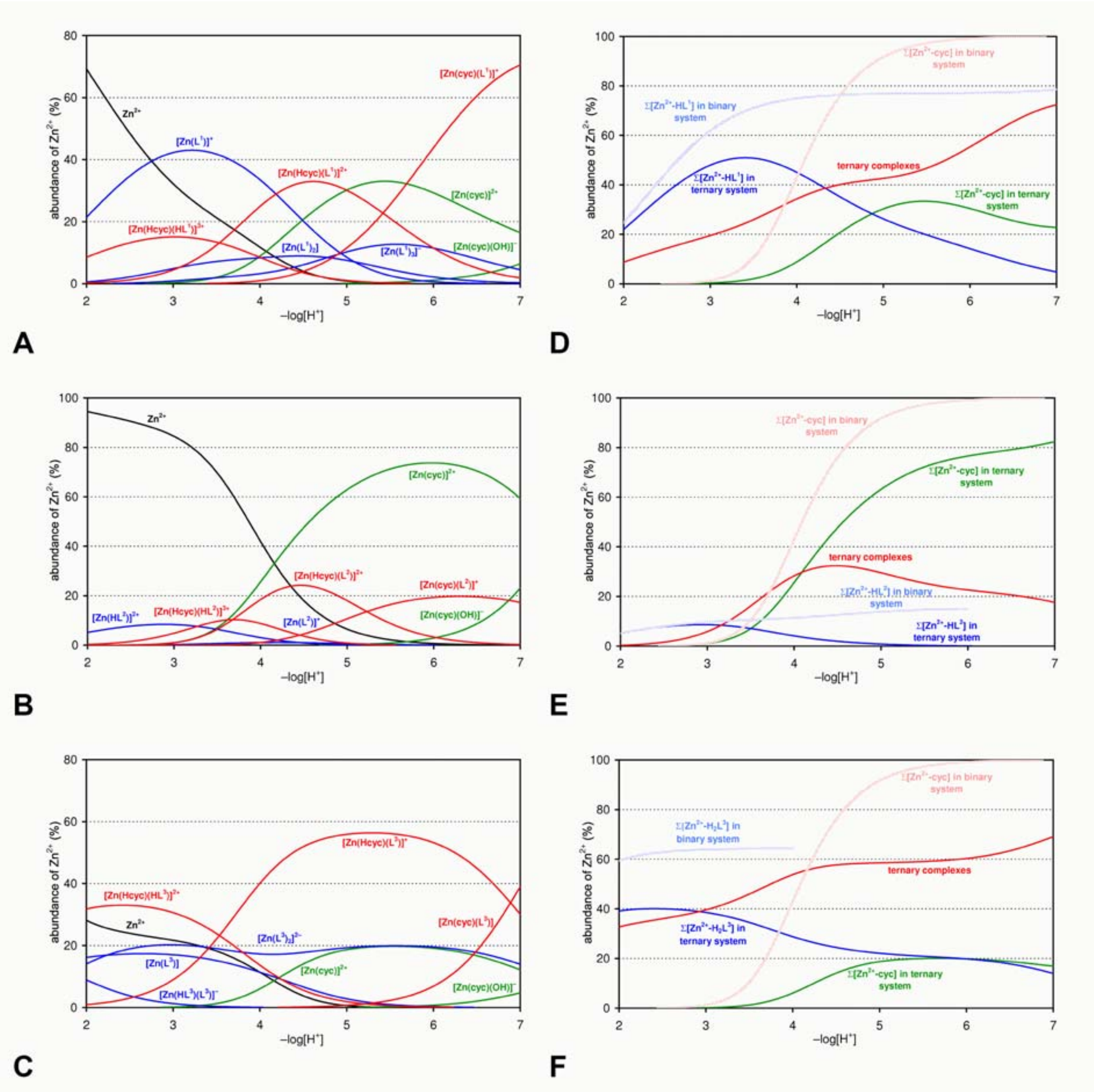

Fig. 7

A) Abundance of cyclen-containing species the Zn^{2+}:cyclen:HL^1 = 1:1:1 system; $c(Zn^{2+})$ = 0.004 mol dm^{-3}; ternary species (red), binary species (green). B) Comparison of sum of ^1H NMR signal integral intensities of protonated cyclen species (red diamonds) with total abundance of the protonated cyclam species (black line) and the deprotonated $[Zn(cyclen)]^{2+}$ complex (violet line) calculated from potentiometry.