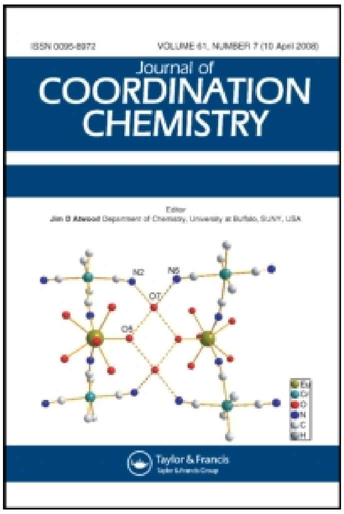

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THE CRYSTAL AND MOLECULAR STRUCTURE OF A FURAN-2-CARBOXYLATE HETEROBIMETALLIC COMPLEX $[Zn(H_2O)_6]^{2+}[Zn_8Na_2(C_5H_3O_3)_{18}(OH)_2]^{2-}$

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The crystals of a zinc-sodium complex with furan-2-carboxylate (FCA) as a ligand, $n[Zn(H_2O)_6]^{2+}[Zn_8Na_2(FCA)_{18}(OH]_2]_n^{2-}$, contain hexahydrated zinc cations and polyanions in which four differently coordinated zinc(II) cations are bridged by bidentate and monodentate (FCA) ligands. In addition, a number of carboxylate and furan ring oxygen atoms are coordinated to sodium(I) atoms which constitute the backbone of the polyanion. $[Zn(H_2O)_6]^{2+}$ cations are located in cavities formed by adjacent polyanions and interact with them *via* a system of hydrogen bonds. The resulting molecular layers are stacked in the crystal along the [100] direction.

Keywords: Zinc complexes; Sodium complexes; Furan-2-carboxylic acid; X-ray crystal structure analysis

INTRODUCTION

Rapidly growing interest in zinc containing enzymes and drugs stimulates studies of crystal-chemical properties of its complexes, particularly those containing metal-heteroring oxygen ligands. Owing to its electronic structure, zinc exhibits flexibility of coordination numbers and coordination polyhedra in its complexes. The d^{10} electron configuration rules out ligand

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*Corresponding author. Tel.: 4822 811 1313, Fax: 4822 811 1917, e-mail: jlec@orange.ichj.waw.pl field stabilizing effects and often leads to a strongly distorted coordination sphere. This effect has been observed in the structures of many zinc containing enzymes, where the metal center of a protein is forced by its relatively rigid environment into unusually distorted coordination. This distortion is associated with strong Lewis acidity of zinc and often brings about high reactivity of the enzyme [1]. In most of its complexes, zinc is six-coordinate, however, compounds with coordination numbers four and five are also known. The flexibility in aquiring different coordination environments leads to efficient and kinetically rapid action of this metal in enzymatic catalysis [2–4]. In fact, a penta-coordinate zinc center was found to be a transient state in catalytic reactions being kinetically more labile than hexa-coordinate [5, 6]. The flexibility of coordination schemes around the zinc(II) cation is well demonstrated by the structures of its complexes with two ligands of the same geometry and almost the same dimensions: furan-2-carboxylate and thiophen-2-carboxylate. In monomeric molecules of zinc thiophenate the metal ion is coordinated by two oxygen atoms donated by water molecules and two oxygen atoms from two monodentate carboxylate groups of the ligands making a distorted tetrahedron [7], while in the structure of the zinc(II) furoate, dimeric molecules are observed in which two zinc(II) ions are connected by three carboxylate bridges. Both show a distorted octahedral enviroment [8]. Keeping in mind the particular preference of zinc(II) and sodium(I) cations to furancarboxylate binding, we performed a number of experiments to synthesize and grow single crystals of a furan-2-carboxylate complex containing both cations. The results of an X-ray diffraction study of its structure are reported in this paper.

EXPERIMENTAL

After a number of preliminary tests, the reaction was carried out by adding 0.113 g of zinc carbonate and 0.031 g of sodium carbonate, both analytical grade, to 100 mL of a hot aqueous solution containing 0.205 g of furan-2-carboxylic acid (ALDRICH). After boiling for an hour the solution was left to crystallize at room temperature. Colorless single crystals of the title complex in the form of flat plates were found in the mother liquid after a few days. The dimensions of the single crystal used to collect X-ray diffraction data are given in Table I.

Intensities of X-ray reflections were measured at room temperature using a KUMA KM4 four circle diffractometer operating in $\omega-2\theta$ scan mode. Two standard reflections were monitored every 200 reflections, and

TABLE I Crystal data and structure refinement details for $n[Zn(H_2O)_6]^{2+}[Zn_8Na_2(FCA)_{18}(OH)_2]_n^{2-}$

Formula	$Zn_9Na_2C_{90}H_{68}O_{62}$
Unit cell weight	2775.72
Temperature	293 K
Wavelength	1.54178 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 12.138(2)$ Å, $\alpha = 103.94(3)°$
	$b = 14.718(3)$ Å, $\beta = 94.95(3)°$
	$c = 15.883(3)$ Å, $\gamma = 73.13(3)°$
V	2635 Å^3
Z	2
Calculated density	1.749 g cm^{-3}
μ (CuKα)	3.26 mm^{-1}
$F(000)$	1396.0
Crystal size	0.4 × 0.4 × 0.3 mm^3
θ range for data collection	2.87 to 65.04°
Index range	$-14 \leq h \leq 14$, $-17 \leq k \leq 16$, $0 \leq l \leq 18$
No. of measured reflections	5880
No. of reflections with $F_o > 4\sigma(F_o)$	5642
Method of structure solution	direct methods
Method of structure refinement	full-matrix least squares on F^2
No. of parameters refined	768
Goodness-of-fit on F^2	1.030
Final R1 index	0.039
Final wR2 index	0.099
Absorption correction	Ψ-scan
Min.and max. transmission factors	0.54/0.88
Largest diff. peak and hole	0.43 e/A^3 and -0.53 e/A^3
Weight parameters (A, B)	0.088, 0.00

remained constant throughout the data collection. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections ($18° < 2\theta < 30°$). Reflections were processed using profile analysis and were corrected for Lorentz factor and polarization effects. Absorption correction based on ψ-scan was applied. Non-hydrogen atoms were located by direct methods using the SHELXLS program [9] and hydrogen atoms were then found by successive Fourier syntheses. Final least-squares refinement was performed on F^2. It included positional parameters of all atoms, anisotropic temperature factors for all non H-atoms and isotropic temperature factors for hydrogen atoms. The weighting scheme used was in the form: $w = 1/[\sigma^2(F_o^2) + (A^*P)^2 + B^*P]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$ and A, B were refined parameters listed in Table I. The calculations were carried out using SHELXL97 [10]. Final atomic coordinates and equivalent isotropic displacements are listed in Table II, bond lengths and angles in Table III. Listings of the observed and calculated structure factors and anisotropic thermal parameters are available from the authors on request.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for $n[Zn(H_2O)_6]^{2+}[Zn_8Na_2(FCA)_{18}(OH)_2]_n^{2-}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Zn(1)	0	0	5000	44(1)
Zn(2)	27(1)	3303(1)	8083(1)	39(1)
Zn(3)	−114(1)	1095(1)	8196(1)	43(1)
Zn(4)	−1878(1)	3967(1)	6558(1)	44(1)
Zn(5)	2384(1)	1414(1)	7623(1)	53(1)
O(11)	1319(3)	3629(2)	8917(2)	50(1)
O(21)	2899(3)	2399(2)	8510(2)	64(1)
C(11)	2380(4)	3211(3)	8963(3)	47(1)
C(21)	3087(4)	3717(3)	9595(3)	50(1)
O(31)	2559(3)	4562(3)	10131(2)	77(1)
C(31)	3364(8)	4853(6)	10634(5)	101(2)
C(41)	4364(6)	4318(6)	10451(5)	100(2)
C(51)	4220(4)	3467(5)	9730(4)	87(2)
O(12)	−432(2)	3904(3)	6053(2)	59(1)
O(22)	850(3)	3454(2)	7075(2)	53(1)
C(12)	568(4)	3742(3)	6384(3)	44(1)
C(22)	1474(4)	3872(3)	5922(3)	49(1)
O(32)	1304(5)	4270(4)	5228(4)	115(2)
C(32)	2449(7)	4206(6)	4989(5)	105(2)
C(42)	3159(6)	3790(6)	5504(6)	104(2)
C(52)	2585(4)	3585(4)	6112(3)	56(1)
O(13)	−844(2)	4818(2)	8354(2)	47(1)
O(23)	−2216(3)	5230(2)	7362(2)	56(1)
C(13)	−1617(4)	5406(3)	8050(3)	43(1)
C(23)	−1942(3)	6446(3)	8489(3)	47(1)
O(33)	−1317(3)	6730(2)	9218(2)	51(1)
C(33)	−1767(4)	7704(3)	9490(3)	63(1)
C(43)	−2614(4)	8029(3)	8979(4)	73(2)
C(53)	−2739(4)	7225(3)	8319(4)	70(2)
O(14)	−719(3)	3252(2)	9205(2)	55(1)
O(24)	−799(3)	1802(2)	9349(2)	58(1)
C(14)	−957(3)	2706(3)	9608(3)	44(1)
C(24)	−1452(4)	3150(3)	10482(3)	52(1)
O(34)	−1344(3)	4073(2)	10865(2)	67(1)
C(34)	−1847(6)	4363(4)	11634(4)	84(2)
C(44)	−2290(6)	3684(5)	11766(4)	98(2)
C(54)	−2032(5)	2868(5)	11004(4)	82(2)
O(15)	−1512(2)	3028(2)	7305(2)	43(1)
O(25)	−1729(3)	1698(2)	7639(3)	68(1)
C(15)	−2128(4)	2495(3)	7459(3)	46(1)
C(25)	−3375(4)	2905(3)	7451(3)	52(1)
O(35)	−3839(3)	3807(3)	7312(2)	67(1)
C(35)	−4998(5)	4018(5)	7353(5)	93(2)
C(45)	−5265(6)	3268(8)	7517(6)	125(3)
C(55)	−4224(6)	2522(6)	7570(5)	96(2)
O(16)	1332(3)	528(2)	8905(2)	59(1)
O(26)	2923(3)	273(2)	8160(3)	71(1)
C(16)	2386(4)	169(3)	8761(3)	53(1)
C(26)	3079(4)	−399(3)	9358(4)	63(1)
O(36)	2461(4)	−504(3)	10014(3)	82(1)
C(36)	3249(8)	−929(5)	10557(6)	115(3)
C(46)	4306(7)	−1101(6)	10272(7)	126(3)

TABLE II (Continued)

	x	y	z	U_{eq}
C(56)	4181(5)	−755(4)	9479(6)	105(3)
O(17)	−1982(3)	2471(2)	5104(2)	58(1)
O(27)	−3013(2)	3988(2)	5628(2)	47(1)
C(17)	−2784(3)	3201(3)	5040(3)	43(1)
C(27)	−3499(3)	3205(3)	4256(3)	44(1)
O(37)	−4461(4)	3903(3)	4133(4)	99(1)
C(37)	−4832(6)	3532(6)	3248(5)	93(2)
C(47)	−4127(7)	2687(7)	2968(4)	104(3)
C(57)	−3288(4)	2444(3)	3568(3)	47(1)
O(18)	2143(4)	1278(3)	5538(3)	96(1)
O(28)	3343(3)	1275(3)	6691(3)	78(1)
C(18)	3082(5)	1272(4)	5907(4)	68(2)
C(28)	4019(6)	1244(4)	5357(4)	78(2)
O(38)	3899(6)	1232(5)	4501(5)	152(2)
C(38)	4992(10)	1228(8)	4252(8)	153(5)
C(48)	5684(8)	1219(6)	4941(8)	130(4)
C(58)	5089(4)	1241(4)	5622(5)	77(2)
O(19)	−51(3)	−176(2)	7375(2)	69(1)
O(29)	−504(4)	−516(3)	8565(3)	91(1)
C(19)	−255(5)	−752(3)	7788(4)	65(1)
C(29)	−190(5)	−1740(3)	7282(3)	63(1)
O(39)	111(4)	−1989(3)	6436(2)	87(1)
C(39)	131(6)	−2943(4)	6148(4)	85(2)
C(49)	−164(6)	−3284(4)	6743(4)	98(3)
C(59)	−302(7)	−2530(4)	7504(4)	94(2)
O(1)	−1189(3)	600(2)	4138(2)	55(1)
O(2)	32(3)	1379(2)	5786(2)	50(1)
O(3)	−1403(3)	83(3)	5730(3)	62(1)
O(4)	704(2)	1792(2)	7620(2)	42(1)
Na(5)	0	5000	10000	108(1)
Na(6)	0	0	10000	99(1)

TABLE III Selected bond lengths (Å) and angles (°) for $[Zn(H_2O)_6]^{2+}[Zn_8Na_2(FCA)_{18}(OH)_2]^{2-}$

Distance [*Å*]		*Angle* [°]	
Hexaqua zinc(II) cation			
Zn(1)-O(1) [-O(1)$^{(III)}$]	2.059(3)	O(1)-Zn(1)-O(2)	93.3(1)
Zn(1)-O(2) [-O(2)$^{(III)}$]	2.121(3)	O(2)-Zn(1)-O(3)	87.4(1)
Zn(1)-O(3) [-O(3)$^{(III)}$]	2.100(4)	O(3)-Zn(1)-O(1)	87.0(1)
Zn trimer			
Zn(2)-Zn(3)	3.351(1)		
Zn(2)-Zn(5)	3.348(1)		
Zn(5)-Zn(3)	3.428(1)		
Zn(2)-O(4)	2.102(3)	Zn(2)-O(4)-Zn(3)	108.8(1)
Zn(3)-O(4)	2.018(3)	Zn(3)-O(4)-Zn(5)	119.4(1)
Zn(5)-O(4)	1.952(3)	Zn(5)-O(4)-Zn(2)	111.3(1)
Zn(2) coordination			
Zn(2)-O(4)	2.102(3)	O(4)-Zn(2)-O(13)	170.0(1)
Zn(2)-O(11)	2.053(3)	O(11)-Zn(2)-O(15)	173.5(1)

TABLE III (Continued)

Distance [*Å*]		*Angle* [°]	
Zn(2)–O(22)	2.047(3)	O(14)–Zn(2)–O(22)	173.6(1)
Zn(2)–O(13)	2.127(3)	O(13)–Zn(2)–O(22)	90.2(1)
Zn(2)–O(25)	2.232(3)	O(13)–Zn(2)–O(14)	86.9(1)
Zn(3) coordination			
Zn(3)–O(4)	2.018(3)	O(4)–Zn(3)–O(16)	93.8(1)
Zn(3)–O(16)	2.075(3)	O(4)–Zn(3)–O(24)	117.0(1)
Zn(3)–O(24)	1.992(3)	O(24)–Zn(3)–O(25)	87.2(1)
Zn(3)–O(25)	2.117(3)	O(19)–Zn(3)–O(25)	88.7(1)
Zn(3)–O(19)	1.199(3)	O(19)–Zn(3)–O(16)	94.3(1)
Zn(4) coordination			
Zn(4)–O(12)	1.960(3)	O(23)–Zn(4)–O(27)	109.7(1)
Zn(4)–O(27)	1.931(3)	O(23)–Zn(4)–O(12)	102.0(1)
Zn(4)–O(15)	1.965(3)	O(12)–Zn(4)–O(15)	107.3(1)
Zn(4)–O(23)	1.938(3)	O(12)–Zn(4)–O(27)	106.7(1)
Zn(5) coordination			
Zn(5)–O(4)	1.952(3)	O(4)–Zn(5)–O(26)	107.1(1)
Zn(5)–O(21)	1.996(3)	O(4)–Zn(5)–O(28)	127.1(2)
Zn(5)–O(26)	1.984(4)	O(4)–Zn(5)–O(21)	107.8(1)
Zn(5)–O(28)	1.900(4)	O(26)–Zn(5)–O(21)	100.5(1)
Na(5) coordination			
Na(5)–O(11)[–O(11)$^{\mathrm{I}}$]	2.554(3)	O(11)–Na(5)–O(13)	67.0(1)
Na(5)–O(13)[–O(13)$^{\mathrm{I}}$]	2.705(3)	O(11)–Na(5)–O(14)	60.7(1)
Na(5)–O(14)[–O(14)$^{\mathrm{I}}$]	2.919(3)	O(13)–Na(5)–O(14)	62.0(1)
Na(5)–O(31)[–O(31)$^{\mathrm{I}}$]	2.923(4)	O(11)–Na(5)–O(34)	106.9(1)
Na(5)–O(34)[–O(34)$^{\mathrm{I}}$]	2.999(4)	O(11)–Na(5)–O(31)	57.8(1)
		O(31)–Na(5)–O(34)	123.1(1)
Na(6) coordination			
Na(6)–O(29)[–O(29)$^{\mathrm{II}}$]	2.311(4)	O(36)–Na(6)–O(16)	55.0(1)
Na(6)–O(16)[–O(16)$^{\mathrm{II}}$]	2.849(4)	O(16)–Na(6)–O(24)	56.6(1)
Na(6)–O(24)[–O(24)$^{\mathrm{II}}$]	2.950(3)	O(16)–Na(6)–O(29)	70.2(1)
Na(6)–O(36)[–O(36)$^{\mathrm{II}}$]	2.861(4)		
Na–Zn distances			
Na(5)–Zn(2)[–Zn(2)$^{\mathrm{I}}$]	3.438(1)		
Na(6)–Zn(3)[–Zn(3)$^{\mathrm{II}}$]	3.585(1)		
Furan-2-carboxylate (FCA) ligands			
FCA1			
C(21)–O(31)	1.346(3)	C(51)–C(21)–O(31)	112.1(5)
O(31)–C(31)	1.312(7)	C(21)–O(31)–C(31)	106.6(5)
C(31)–C(41)	1.254(10)	O(31)–C(31)–C(41)	113.9(7)
C(41)–C(51)	1.521(10)	C(31)–C(41)–C(51)	105.7(5)
C(51)–C(21)	1.329(7)	C(41)–C(51)–C(21)	101.5(5)
C(21)–C(11)	1.471(6)		
C(11)–O(11)	1.260(5)	O(11)–C(11)–O(21)	125.9(4)
C(11)–O(21)	1.253(5)		
FCA 2			
C(22)–O(32)	1.342(6)	C(51)–C(21)–O(31)	110.6(4)
O(32)–C(32)	1.443(8)	C(22)–O(32)–C(32)	104.1(5)
C(32)–C(42)	1.265(10)	O(32)–C(32)–C(42)	108.1(6)

TABLE III (Continued)

Distance [Å]		*Angle* [°]	
C(42)-C(52)	1.373(8)	C(32)-C(42)-C(52)	110.2(6)
C(52)-C(22)	1.322(6)	C(42)-C(52)-C(22)	106.9(5)
C(22)-C(12)	1.454(6)		
C(12)-O(12)	1.260(5)	O(12)-C(12)-O(22)	124.9(4)
C(12)-O(22)	1.255(5)		
FCA 3			
C(23)-O(33)	1.375(5)	C(53)-C(23)-O(33)	109.4(4)
O(33)-C(33)	1.352(5)	C(23)-O(33)-C(33)	106.2(4)
C(33)-C(43)	1.305(7)	O(33)-C(33)-C(43)	110.7(4)
C(43)-C(53)	1.415(7)	C(33)-C(43)-C(53)	107.6(4)
C(53)-C(23)	1.337(6)	C(43)-C(53)-C(23)	106.1(5)
C(23)-C(13)	1.472(5)		
C(13)-O(13)	1.231(5)	O(13)-C(13)-O(23)	127.3(4)
C(13)-O(23)	1.274(5)		
FCA 4			
C(24)-O(34)	1.387(5)	C(54)-C(24)-O(34)	109.7(4)
O(34)-C(34)	1.331(6)	C(24)-O(34)-C(34)	108.1(4)
C(34)-C(44)	1.328(9)	O(34)-C(34)-C(44)	110.1(5)
C(44)-C(54)	1.466(9)	C(34)-C(44)-C(54)	107.4(5)
C(54)-C(24)	1.338(7)	C(44)-C(54)-C(24)	104.6(5)
C(24)-C(14)	1.481(6)		
C(14)-O(14)	1.247(5)	O(14)-C(14)-O(24)	126.1(4)
C(14)-O(24)	1.265(5)		
FCA 5			
C(25)-O(35)	1.347(6)	C(55)-C(25)-O(35)	109.7(5)
O(35)-C(35)	1.353(6)	C(25)-O(35)-C(35)	108.2(5)
C(35)-C(45)	1.328(9)	O(35)-C(35)-C(45)	109.0(6)
C(45)-C(55)	1.425(10)	C(35)-C(45)-C(55)	108.2(5)
C(55)-C(25)	1.355(7)	C(45)-C(55)-C(25)	104.9(6)
C(25)-C(15)	1.481(6)		
C(15)-O(15)	1.247(5)	O(15)-C(15)-O(25)	124.5(4)
C(15)-O(25)	1.224(5)		
FCA 6			
C(26)-O(36)	1.396(7)	C(56)-C(26)-O(36)	100.5(6)
O(36)-C(36)	1.349(8)	C(26)-O(36)-C(36)	106.4(6)
C(36)-C(46)	1.331(12)	O(36)-C(36)-C(46)	110.1(8)
C(46)-C(56)	1.450(12)	C(36)-C(46)-C(56)	106.8(6)
C(56)-C(26)	1.304(8)	C(46)-C(56)-C(26)	106.1(7)
C(26)-C(16)	1.463(7)		
C(16)-O(16)	1.253(5)	O(16)-C(16)-O(26)	126.1(5)
C(16)-O(26)	1.263(6)		
FCA 7			
C(27)-O(37)	1.346(6)	C(57)-C(27)-O(37)	112.0(4)
O(37)-C(37)	1.470(8)	C(27)-O(37)-C(37)	103.3(5)
C(37)-C(47)	1.287(10)	O(37)-C(37)-C(47)	107.0(5)
C(47)-C(57)	1.364(9)	C(37)-C(47)-C(57)	111.8(6)
C(57)-C(27)	1.344(6)	C(47)-C(57)-C(27)	105.8(5)
C(27)-C(17)	1.456(6)		
C(17)-O(17)	1.240(5)	O(17)-C(17)-O(27)	123.4(4)
C(17)-O(27)	1.276(5)		

TABLE III (Continued)

Distance [Å]		Angle [°]	
FCA 8			
C(28)-O(38)	1.352(8)	C(58)-C(28)-O(38)	109.8(6)
O(38)-C(38)	1.415(10)	C(28)-O(38)-C(38)	104.7(8)
C(38)-C(48)	1.321(14)	O(38)-C(38)-C(48)	108.0(8)
C(48)-C(58)	1.340(10)	C(38)-C(48)-C(58)	108.8(8)
C(58)-C(28)	1.329(8)	C(48)-C(58)-C(28)	108.6(8)
C(28)-C(18)	1.478(7)		
C(18)-O(18)	1.233(7)	O(18)-C(18)-O(28)	128.0(5)
C(18)-O(28)	1.258(7)		
FCA 9			
C(29)-O(39)	1.358(6)	C(59)-C(29)-O(39)	108.6(4)
O(39)-C(39)	1.361(6)	C(29)-O(39)-C(39)	106.0(4)
C(39)-C(49)	1.290(7)	O(39)-C(39)-C(49)	111.9(4)
C(49)-C(59)	1.414(7)	C(39)-C(49)-C(59)	105.9(4)
C(59)-C(29)	1.338(7)	C(49)-C(59)-C(29)	107.4(5)
C(29)-C(19)	1.466(6)		
C(19)-O(19)	1.276(6)	O(19)-C(19)-O(29)	123.8(4)
C(19)-O(29)	1.237(6)		

Hydrogen bonds

	Distance (*D*-*A*) [Å]	Distance (*H*-*A*) [Å]	Angle (*D*-*H*-*A*) [°]
O(1)-H(11)···O(19)^{III}	2.79(1)	1.85(1)	160.6(1)
O(1)-H(11)···O(39)^{III}	3.06(1)	2.51(1)	115.9(1)
O(1)-H(21)···O(17)	2.75(1)	1.78(1)	168.5(1)
O(2)-H(12)···O(18)	2.58(1)	1.62(1)	167.5(1)
O(2)-H(22)···O(17)	2.80(1)	1.88(1)	155.2(1)
O(3)-H(13)···O(18)^{III}	2.77(1)	1.91(1)	144.9(1)
O(3)-H(23)···O(25)	3.34(1)	2.52(1)	141.0(1)
O(4)-H(14)···O(2)	2.92(1)	2.00(1)	175.9(1)

Symmetry codes: (^{I}): $-x, -y+1, -z+2$; (^{II}): $-x, -y, -z+2$; (^{III}): $-x, -y, -z+1$.

DISCUSSION

The crystals of the title compound contain $[Zn(H_2O)_6]^{2+}$ cations and polymeric anions $[Zn_8Na_2(FCA)_{18}(OH)_2]^{2-}$. The latter are in the form of molecular ribbons propagating in the [010] direction in the crystal. The "backbone" of each ribbon is composed of sodium atoms located in the symmetry centers in the 0,0,0 and 0,1/2,0 sites (see, Tab. II). Figure 1 illustrates how this polyanionic ribbon is situated in the unit cell. For clarity, only two polyanions and two $[Zn(H_2O)_6]^{2+}$ cations are shown. The asymmetric unit of the polyanion with numbering of metal ions and furan-2-carboxylate ligands and a $[Zn(H_2O)_6]^{2+}$ cation are displayed in Figure 2. Inside the polyanion, sodium ions are linked along a bridging

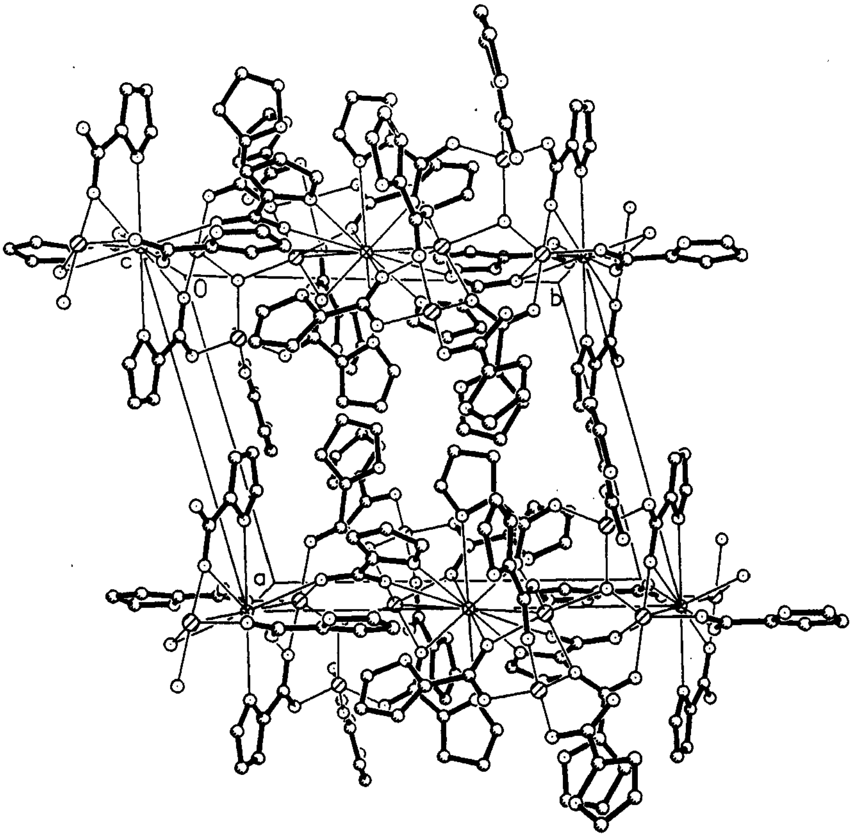

FIGURE 1 Two $[Zn_8Na_2(FCA)_{18}(OH)_2]_n^{2-}$ polyanions in the unit cell viewed along the *c* axis. For clarity, the hydrogen atoms are not shown.

pathway constituted by zinc and oxygen atoms: –Na5–O11–Zn2–O4–Zn3–O16–Na6–O16^{II}–*etc.* The corresponding bond lengths and angles are given in Table III. The ribbons stacked along the [001] direction form cavities around the symmetry centers located in the 0,0,1/2 sites. These cavities are occupied by the $[Zn(H_2O)_6]^{2+}$ cations which link adjacent ribbons *via* hydrogen bonds donated by the coordinated water molecules. Molecular layers stack in the [100] direction and are held together by weak van der Waals type interactions.

An interesting structural feature of the polyanion is the presence of trimeric moieties composed of zinc(II) ions grouped in a ring with an oxygen atom in its center, triply bridged to the zinc ions. This oxygen atom is located at 0.557 Å above the best plane defined by the zinc atoms, which

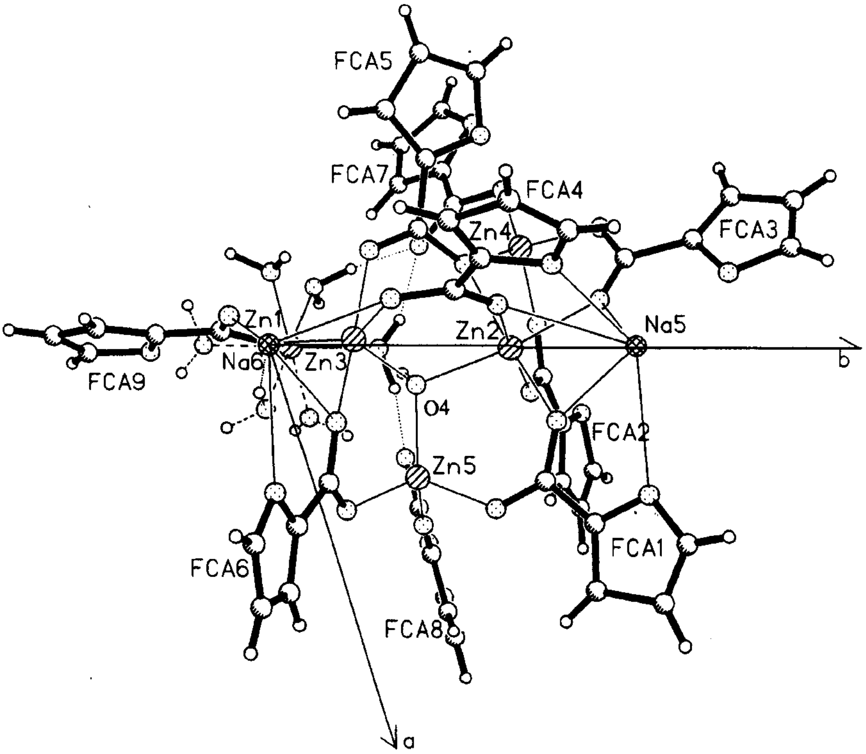

FIGURE 2 The structure of the $[Zn_8Na_2(FCA)_{18}(OH)_2]_n^{2-}$ polyanion with numbering of Zn(II) and Na(I) ions. O4 is the triply coordinated oxygen atom. The numbering of furan-2-carboxylate ligands refers to Table III. For clarity, the positions of hydrogen atoms are not shown.

form a nearly equilateral triangle with an average side of 3.375(1) Å. Although this is not the exact Zn–Zn bonding distance, it is close to the essential one for the metal–metal interaction as observed in some zinc as well as other 3-*d* metal complexes [11]. An inspection of the interatomic distances listed in Table III reveals, that Na(1)–Zn(2) and Na(2)–Zn(3) distances are also shorter than the sum of respective van der Waals radii. The nature of the enviroment around metal ions in these moieties is thus the most important factor influencing the rate of intramolecular electron transfer. Consequently, the oxo – centered metal complexes are often mixed valence and show weak antiferromagnetic exchange interactions [12–14]. Each zinc(II) ion in the trimeric unit is coordinated by the furan-2-carboxylate ligands and exhibits different coordination: Zn(5)-tetrahedral, Zn(3)-pentagonal and Zn(2)-octahedral (Fig. 2). The coordination polyhedron is rather distorted in each case, mostly due to steric strains. Detailed bond distances and angles are listed in Table III. Furan-2-carboxylate ligands act as bidentate bridges for most zinc ions. Only two (FCA 7 and FCA 8) are monodentately bonded to the Zn(4) and Zn(5) being simultaneously attached by hydrogen bonds to the hexahydrated zinc ions. Na(I) cations, due to the flexibility of their coordination spheres, are bonded not only to the carboxylate oxygen atoms, but to the hetero-oxygen atoms of the furan ring as well. Na(I) cations are located in the symmetry centers and coordinate either ten oxygen atoms [Na(5)] or 8 oxygens [Na(6)] with the average $Na-O_{carbonyl}$ and $Na-O_{heteroring}$ bond distances of 2.714(4) and 2.928(4) Å, respectively.

The coordination around the hexahydrated Zn(II) ion is octahedral with mean $Zn-O_{water}$ bond distances of 2.093(3) Å. Each coordinated water molecule is linked by a hydrogen bond to the oxygen atom belonging to the carboxylic groups and to the oxygen atoms situated in the centers of the triangle composed of zinc ions. The respective bond lengths and angles are given in Table III.

The title compound is an example of a complex in which a number of several types of bonding modes are operative. These are: metal-carboxylate oxygen mono and bidentate bonds, tridentate metal–oxygen bonds, metal–heteroring oxygen bonds and hydrogen bonds. An interesting feature is the coexistance of the zinc(II) ions with four, five and six coordination, in addition to the hexaaquo zinc cations with almost regular octahedral coordination. The other feature is the highly irregular coordination geometry with coordination numbers of eight and ten around sodium ions which show distinctive bonds to the oxygen atoms of the furan rings. The same property of the furan heteroring oxygen atom has already been observed in the structures of alkaline metal complexes with furan-2-carboxylate and furan-3-carboxylate ligands [15–17].

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References

[1] B. L. Vallee and R. J. P. Williams, *Proc. Natl. Acad. Sci. USA* **59**, 498 (1968).

[2] R. J. P. Williams, *Pure Appl. Chem.* **54**, 1889 (1982).

[3] R. H. Woolley, *Angew. Chem.* **84**, 461 (1972).

[4] P. C. Rees, W. Lewis and J. Lipscomb, *J. Am. Chem. Soc.* **106**, 463 (1984).
[5] L. C. Kuo and M. W. Mankinen, *J. Biol. Chem.* **257**, 24 (1982).
[6] R. T. Dworschak and B. V. Plapp, *Biochem.* **16**, 111 (1977).
[7] B. Paluchowska, J. K. Maurin and J. Leciejewicz, to be published.
[8] B. Paluchowska, J. K. Maurin and J. Leciejewicz, *Polish J. Chem.* **72**, 2172 (1998).
[9] G. M. Sheldrick, *Acta Cryst.* **A46**, 467 (1990).
[10] G. M. Sheldrick, SHELXL 97, *Program for crystal structure refinement.* University of Goettingen, Germany 1997.
[11] W. Clegg, D. R. Harbron, C. D. Homan, P. A. Hunt, I. R. Little and B. P. Straughan, *Inorg. Chim. Acta* **186**, 51 (1991).
[12] S. M. Oh, D. N. Hendrickson, K. L. Hassett and R. E. Davies, *J. Am. Chem. Soc.* **106**, 7984 (1984).
[13] A. R. E. Baikie, M. B. Hursthouse, L. New, P. Thornton and R. G. White, *J. Chem. Soc., Chem. Comm.*, p. 684 (1980).
[14] S. E. Woehler and R. J. Wittebort, *J. Am. Chem. Soc.* **109**, 1063 (1987).
[15] B. Paluchowska, J. K. Maurin and J. Leciejewicz, *Acta Cryst.* **C52**, 347 (1996).
[16] B. Paluchowska, J. K. Maurin and J. Leciejewicz, *Polish J. Chem.* **70**, 1402 (1996).
[17] B. Paluchowska, J. K. Maurin and J. Leciejewicz, *Acta Cryst.* **C53**, 287 (1997).