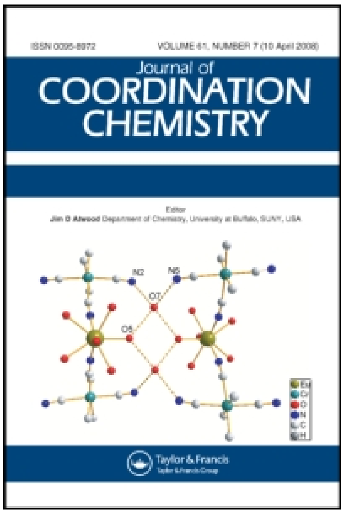

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X-RAY DIFFRACTION STUDY ON MANGANESE(II) COMPLEXES WITH THIOPHENE-2-CARBOXYLATE AND FURAN-3-CARBOXYLATE LIGANDS

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Mn(II) cations in the crystals of trisaquobis(μ-thiophen-2-carboxylato-O,O′)(thiophen-2-carboxylato-O)manganese(II) monohydrate are bridged by oxygen atoms donated by bidentate carboxylic groups of two thiophen-2-carboxylate ligands. In addition, each Mn(II) ion is coordinated by an oxygen atom of a monodentate carboxylic group of this ligand and three oxygen atoms of water molecules. The coordination around the Mn(II) cation is octahedral. The bridging of the ligands results in molecular ribbons propagating in the *c*-direction of the crystal held together by C–H$\cdots$O hydrogen bonds. The crystal structure of diaquobis(μ-furan-3-carboxylato-O,O′)di(μ-furan-3-carboxylato-O,O)(μ-aqua-O)manganese(II) consists of dinuclear structural units. In each molecule Mn(II) cations are *O, O′* bridged by oxygen atoms of bidentate carboxylic groups of two furan-3-carboxylate ligands and have a water located between the Mn cations. The units are *O,O′* bridged to Mn(II) ions located in adjacent units by bidentate oxygen atoms, forming molecular ribbons extending in the *c*-direction. Octahedral coordination around each Mn(II) ion is completed by two water molecules. The octahedra around two adjacent metal ions in the unit share a common apex – the bridging oxygen atom of the water molecule. The ribbons are held together by C–H$\cdots$O hydrogen bonds between furan ring oxygen atoms and the carbon atoms of adjacent furan rings.

Keywords: Thiophene-2-carboxylic acid; furan-3-carboxylic acid; manganese complex; X-ray structure analysis

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INTRODUCTION

It is well known that thiophene has more aromatic character than furan. According to Pauling, the electronegativity of sulfur (2.5) is lower than that of oxygen (3.5). Although in sulfur the electron lone pair also occupies *p*-orbitals as in oxygen, it was suggested that thiophene differs from furan by having low-lying, empty *d*-orbitals which could take part in bond formation. The *ab initio* calculations clearly show that sulfur in a thiazole ring has a net positive charge, which results from donation of p_z electrons to the π system of the heterocycle. The *d*-orbitals on sulfur may act as an extra polarization factor. The molecular electrostatic isopotential maps calculated for sulfur and oxygen in heterocyclic rings in some molecules show regions of positive potential around the sulfur heteroatom and a region of negative potential around oxygen. Thus the sulfur–metal interaction can be interpreted as an electrostatic repulsion between the positively charged thiazole sulfur atom and the metal cation.

There is evidence based on the electronic structure of the five-membered heterocyclic ring, that heteroring atoms like oxygen and sulfur act as potential electron donors when binding metal cations during complexation. This effect was observed in the structures of alkaline earth metals complexed with furan-2-carboxylate and furan-3-carboxylate ligands.[1] There is, however, no information on multidentate sulfur and oxygen ligands with the thiophene ring and carboxylic group as chelating sites.[2] Having a similar valence orbital configuration to oxygen, the sulfur heteroatom was reported as not showing any bonding interactions with metals in the process of coordination by ligands containing a thiophene ring.[2] For example, our previous studies indicated that Cu^{2+} and Zn^{2+} thiophenates[3,4] do not exhibit any close contacts between the heteroring sulfur and the metal cation. Therefore, as a continuation in our ongoing structural studies of complexes formed by 3-*d* metal cations with the heterocyclic carboxylic ligands, we have determined the crystal structures of the title compounds.

EXPERIMENTAL

Both title compounds were prepared by adding 1 millimol of manganese carbonate (analytical grade) to 50 mL of warm aqueous solution of 2 millimols of thiophene-2-carboxylic acid (Aldrich) or 2 millimols of furan-3-carboxylic acid (Aldrich). Colorless single crystals of both title compounds were formed after a few days. The dimensions of the single crystals used for data collection are given in Table I.

TABLE I Crystal data and structure refinement details

Identification code	$Mn(TCA)_2(H_2O)_3 \cdot H_2O$	$Mn_2(FCA)_4(H_2O)_6$
Empirical formula	$C_{10}H_{14}MnO_8S_2$	$C_{20}H_{18}Mn_2O_{15}$
Formula weight	381.27	608.22
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic
Space group	P2(1)/c	$P\bar{1}$
Unit cell dimensions	$a = 15.659(3)$ Å,	$a = 7.780(2)$ Å, $\alpha = 110.98(3)^\circ$
	$b = 10.487(2)$ Å, $\beta = 99.13(3)$	$b = 10.640(2)$ Å, $\beta = 106.90(3)^\circ$
	$c = 9.372(2)$ Å,	$c = 15.670(3)$ Å $\gamma = 90.08(3)^\circ$
Volume	1519.5(5) $Å^3$	1150.7(4) $Å^3$
Z	4	2
Calculated density	1.667 Mg/m^{-3}	1.755 Mg/m^{-3}
Absorption coefficient	1.176 mm^{-1}	1.176 mm^{-1}
$F(000)$	780	616
Crystal dimensions (in mm)	$0.3 \times 0.3 \times 0.4$	$0.2 \times 0.3 \times 0.2$
θ range for data collection	2.35–34.99°	2.04 to 35.23°
Index ranges	$-20 \leq h \leq 20, 0 \leq k \leq 16,$ $0 \leq l \leq 15$	$-12 \leq h \leq 11,$ $-16 \leq k \leq 17, -25 \leq l \leq 0$
Reflections collected/unique	6642/6341	10319/10005
R(int)	0.0401	0.0566
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6341/12/215	10005/9/352
Goodness-of-fit on F^2	0.840	0.891
Weighting scheme	$A = 0.0730, B = 1.3329$	$A = 0.0941, B = 0.3660$
Final R indices [$I > 2\text{sigma}(I)$]	R1 = 0.0428, wR2 = 0.1166	R1 = 0.0483, wR2 = 0.1217
R indices (all data)	R1 = 0.2135, wR2 = 0.1511	R1 = 0.1000, wR2 = 0.1335
Largest diff. peak and hole	0.849 and $-0.783\ e \cdot Å^{-3}$	1.742 and $-0.739\ e \cdot Å^{-3}$
Absorption parameters	$t_{min} = 0.496\ t_{max} = 0.987$	$t_{min} = 0.336\ t_{max} = 0.700$

X-ray reflections were measured at room temperature using a KUMA KM4 (MoK_α radiation) four circle diffractometer operating in the $\omega-2\theta$ scan mode. Two standard reflections were monitored every 200 reflections. They remained constant throughout the data collection. Unit cell dimensions were obtained by least-squares fit to 25 reflections ($15^\circ < 2\theta < 30^\circ$). Reflections were processed using profile analysis and corrected for Lorentz factor and polarization effects; those with $I > 2\sigma(I)$ were used in the structure refinement.

An empirical absorption correction based on Ψ-scans was applied (min. and max. transmission parameters are listed in Table I). Non-hydrogen atoms were located by direct methods using the SHELXS program.[5] The hydrogen atoms were then found by successive difference Fourier syntheses. Models were refined by a least-squares method using SHELX97.[6] In the last cycles of refinement all positional parameters, anisotropic displacement parameters for non-hydrogen atoms and isotropic for hydrogens were included. The weighting scheme used was in the form:

$$w = 1/[\sigma^2(F_o^2) + (A * P)^2 + B * P], \quad \text{where } P = \mathrm{Max}[(F_o^2, 0) + 2F_c^2)]/3.$$

A, B are refined parameters listed in Table I. Final atomic coordinates and equivalent isotropic displacements are listed in Tables II and III; bond lengths and angles in Tables IV and V. Listings of the observed and calculated structure factors and anisotropic thermal parameters can be obtained on request from the authors.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathrm{\AA}^2 \times 10^3$) for $Mn(TCA)_2(H_2O)_3 \cdot H_2O$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Mn1	0.87432(2)	0.32612(3)	0.47359(3)	0.02434(6)
O11	0.86232(11)	0.69826(17)	0.4115(2)	0.0456(5)
O12	0.86664(10)	0.49662(15)	0.34336(18)	0.0372(4)
C11	0.83469(13)	0.6079(2)	0.3314(2)	0.0307(5)
C12	0.76339(14)	0.6324(2)	0.2116(2)	0.0341(5)
C13	0.73055(14)	0.7608(2)	0.1612(2)	0.0374(6)
H13	0.7469	0.8401	0.2005	0.045
C14	0.6658(2)	0.7311(4)	0.0337(3)	0.0681(9)
H14	0.6358	0.7953	−0.0214	0.082
C15	0.6522(2)	0.6108(4)	0.0011(3)	0.0680(10)
H15	0.6123	0.5834	−0.0770	0.082
S11	0.71303(6)	0.51161(9)	0.11216(11)	0.0768(3)
O21	0.76940(10)	0.37185(17)	0.58072(15)	0.0334(4)
O22	0.80925(10)	0.26810(17)	0.78540(16)	0.0377(4)
C21	0.75450(12)	0.3262(2)	0.69881(19)	0.0261(4)
C22	0.66548(13)	0.3420(2)	0.7319(2)	0.0299(5)
C23	0.62947(15)	0.2801(3)	0.8368(3)	0.0467(7)
H23	0.6586	0.2220	0.9020	0.056
C24	0.54181(18)	0.3166(4)	0.8325(4)	0.0672(10)
H24	0.5068	0.2842	0.8953	0.081
C25	0.51445(17)	0.4017(3)	0.7298(3)	0.0563(8)
H25	0.4588	0.4353	0.7136	0.068
S21	0.59271(4)	0.44150(7)	0.63207(7)	0.04533(16)
O1	0.90637(11)	0.13329(15)	0.57478(16)	0.0351(4)
H11	0.8840(10)	0.1008(19)	0.6584(12)	0.042
H12	0.8829(13)	0.0860(15)	0.4886(12)	0.042
O2	0.96277(9)	0.41062(15)	0.66109(16)	0.0321(4)
H21	0.9344(9)	0.4656(14)	0.7221(16)	0.039
H22	1.0116(6)	0.4589(15)	0.638(2)	0.039
O3	0.99563(10)	0.29328(15)	0.38320(16)	0.0324(4)
H31	1.0519(6)	0.297(2)	0.4437(17)	0.039
H32	0.9986(15)	0.2200(10)	0.3211(15)	0.039
O4	0.91326(13)	0.93860(17)	0.3720(2)	0.0514(5)
H41	0.8509(5)	0.960(2)	0.354(3)	0.062

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $Mn_2(FCA)_4(H_2O)_6$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Mn1	0.17652(3)	0.07211(2)	0.486240(16)	0.01801(6)
Mn2	0.19181(3)	0.42768(2)	0.512724(16)	0.01805(6)
O11	0.41056(18)	0.20018(13)	0.58821(9)	0.0274(3)
O12	0.3699(2)	0.41823(16)	0.63937(10)	0.0321(3)
C11	0.4371(2)	0.31854(18)	0.65285(10)	0.0207(3)
C12	0.5586(3)	0.33754(19)	0.74773(13)	0.0280(3)
C13	0.5830(4)	0.4525(2)	0.83639(15)	0.0453(6)
H13	0.5264	0.5310	0.8447	0.054
C14	0.6997(6)	0.4228(3)	0.9012(2)	0.0626(9)
H14	0.7391	0.4792	0.9659	0.075
C15	0.6648(4)	0.2470(3)	0.77104(16)	0.0431(5)
H15	0.6709	0.1612	0.7283	0.052
O13	0.7607(3)	0.2993(3)	0.86543(14)	0.0637(7)
O21	0.2068(2)	0.08124(16)	0.35869(11)	0.0349(3)
O22	0.30859(18)	0.30007(14)	0.41119(9)	0.0258(2)
C21	0.2616(2)	0.18168(17)	0.34678(11)	0.0201(3)
C22	0.2741(3)	0.16454(18)	0.25157(12)	0.0262(3)
C23	0.2000(4)	0.0514(2)	0.16364(14)	0.0427(6)
H23	0.1338	−0.0276	0.1547	0.051
C24	0.2456(5)	0.0822(3)	0.09553(16)	0.0556(8)
H24	0.2178	0.0259	0.0311	0.067
C25	0.3537(4)	0.2570(3)	0.23011(16)	0.0410(5)
H25	0.4108	0.3418	0.2743	0.049
O23	0.3394(4)	0.2100(2)	0.13691(13)	0.0579(6)
O31	−0.2567(2)	0.08552(17)	0.34202(10)	0.0395(4)
O32	−0.08555(17)	−0.05242(13)	0.39842(8)	0.0215(2)
C31	−0.1866(2)	−0.02245(18)	0.33057(12)	0.0244(3)
C32	−0.2189(3)	−0.1223(2)	0.23240(12)	0.0292(4)
C33	−0.3319(4)	−0.1155(3)	0.14537(14)	0.0482(6)
H33	−0.3999	−0.0460	0.1383	0.058
C34	−0.3200(5)	−0.2306(3)	0.07524(17)	0.0625(9)
H34	−0.3797	−0.2536	0.0100	0.075
C35	−0.1479(4)	−0.2412(2)	0.20937(14)	0.0431(6)
H35	−0.0694	−0.2716	0.2532	0.052
O33	−0.2076(4)	−0.3090(2)	0.11343(14)	0.0671(7)
O41	0.0712(3)	0.58687(17)	0.34235(10)	0.0399(4)
O42	−0.03306(17)	0.44788(13)	0.39882(8)	0.0212(2)
C41	−0.0121(2)	0.47839(17)	0.32951(10)	0.0233(3)
C42	−0.0886(3)	0.37849(19)	0.23371(12)	0.0271(3)
C43	−0.0745(5)	0.3821(3)	0.14509(14)	0.0484(7)
H43	−0.0141	0.4513	0.1379	0.058
C44	−0.1634(6)	0.2687(3)	0.07628(17)	0.0624(9)
H44	−0.1751	0.2451	0.0115	0.075
C45	−0.1889(4)	0.2588(2)	0.20830(13)	0.0415(5)
H45	−0.2202	0.2287	0.2513	0.050
O43	−0.2368(4)	0.1894(2)	0.11276(13)	0.0630(6)
O1	0.01377(17)	0.24891(12)	0.49964(8)	0.0211(2)
H11	−0.036(3)	0.310(2)	0.5476(13)	0.032
H12	−0.086(2)	0.192(2)	0.4441(12)	0.032
O2	0.3346(2)	0.60405(15)	0.51517(11)	0.0303(3)
H21	0.4676(13)	0.610(3)	0.530(2)	0.046

TABLE III (*Continued*)

	x	y	z	U_{eq}
H22	0.290(3)	0.648(3)	0.4688(18)	0.046
O3	0.3188(2)	−0.10327(15)	0.48564(12)	0.0311(3)
H31	0.426(3)	−0.118(3)	0.464(2)	0.047
H32	0.332(4)	−0.145(3)	0.5338(18)	0.047

TABLE IV Selected interatomic distances (Å) and bond angles (°) in Mn(TCA)$_2$-(H$_2$O)$_3$ · H$_2$O

	Distance		*Angle*
Mn1 ion coordination octahedron			
Mn1 O21	2.112(2)	O21 Mn1 O22^{I}	101.10(6)
Mn1 O22^{I}	2.134(2)	O21 Mn1 O12	95.91(7)
Mn1 O12	2.158(2)	O21 Mn1 O2	88.17(6)
Mn1 O3	2.226(2)	O21 Mn1 O1	98.14(6)
Mn1 O2	2.240(2)	O22 Mn1 O12^{I}	86.54(7)
Mn1 O1	2.256(2)	O22 Mn1 O3^{I}	86.46(6)
		O22 Mn1 O1^{I}	88.72(6)
		O12 Mn1 O3	83.53(6)
		O12 Mn1 O2	95.05(6)
		O3 Mn1 O1	82.82(6)
		O3 Mn1 O2	84.32(6)
		O2 Mn1 O1	87.49(6)
TCA (thiophene-2-carboxylate) 1 ligand			
O11 C11	1.243(3)	C11 O12 Mn1	143.01(16)
O12 C11	1.268(3)	O11 C11 O12	123.6(2)
C11 C12	1.475(3)	O11 C11 C12	118.4(2)
C12 C13	1.491(3)	O12 C11 C12	117.9(2)
C12 S11	1.692(2)	C11 C12 C13	125.5(2)
C13 C14	1.472(4)	C11 C12 S11	121.26(18)
C14 C15	1.307(5)	C13 C12 S11	113.22(16)
C15 S11	1.661(4)	C14 C13 C12	103.0(2)
O21 C21	1.261(2)	C15 C14 C13	117.4(3)
		C14 C15 S11	113.7(2)
		C15 S11 C12	92.69(15)
TCA 2 ligand			
O22 C21	1.243(2)	C21 O21 Mn1	126.66(14)
C21 C22	1.484(3)	C21 O22 Mn1^{II}	162.98(15)
C22 C23	1.372(3)	O22 C21 O21	123.70(19)
C22 S21	1.710(2)	O22 C21 C22	119.46(18)
C23 C24	1.419(4)	O21 C21 C22	116.83(17)
C24 C25	1.332(5)	C23 C22 C21	127.1(2)
C25 S21	1.694(3)	C23 C22 S21	111.52(17)
		C21 C22 S21	121.36(16)
		C22 C23 C24	110.9(2)
		C25 C24 C23	113.6(3)
		C24 C25 S21	112.2(2)
		C25 S21 C22	91.74(13)

TABLE IV (*Continued*)

	Distance (D–H)	*Distance (H–A)*	*Distance (D–A)*	*Angle (D–H–A)*
Hydrogen bonds				
O1 H11 O22	0.970(9)	2.511(19)	3.027(2)	113.2(14)
O1 H12 O4	0.969(8)	1.993(15)	2.803(2)	139.7(17)^{III}
O2 H21 O4	0.968(9)	1.800(10)	2.738(2)	162.2(13)^{IV}
O2 H22 O12	0.969(8)	1.944(9)	2.849(2)	154.5(14)^{V}
O3 H31 O11	0.969(8)	1.753(10)	2.702(2)	165.4(16)^{V}
O3 H32 O2	0.970(8)	2.043(10)	2.972(2)	159.8(18)^{I}
O4 H42 O11	0.983(8)	1.718(11)	2.687(3)	168(2)

Symmetry codes: (*I*) x, $0.5-y$, $-0.5+z$; (*II*) x, $0.5-y$, $0.5+z$; (*III*) x, $y-1$, z; (*IV*) $1.5-y$, $0.5+x$, (*V*) $2-x$, $1-y$, $1-z$.

TABLE V Selected interatomic distances (Å) and bond angles (°) in $Mn_2(FCA)_4(H_2O)_3$

	Distance		*Angle*
Mn1 coordination octahedron			
Mn1 O11	2.114(2)	O11 Mn1 O21	99.85(7)
Mn1 O21	2.115(2)	O11 Mn1 O3	89.71(6)
Mn1 O3	2.170(2)	O21 Mn1 O3	97.42(7)
Mn1 O32^{I}	2.197(2)	O11 Mn1 O32^{I}	90.92(6)
Mn1 O32	2.205(2)	O3 Mn1 O32^{I}	87.45(6)
Mn1 O1	2.251(2)	O21 Mn1 O32	88.14(6)
		O3 Mn1 O32	93.14(6)
		O32 Mn1 O32^{I}	80.81(5)
		O11 Mn1 O1	91.33(6)
		O21 Mn1 O1	89.36(6)
		O32 Mn1 O1^{I}	85.48(5)
		O32 Mn1 O1	84.82(5)
Mn2 coordination octahedron			
Mn2 O12	2.101(2)	O12 Mn2 O22	99.50(6)
Mn2 O22	2.121(2)	O12 Mn2 O2	97.15(7)
Mn2 O2	2.162(2)	O22 Mn2 O2	90.11(6)
Mn2 O42	2.180(2)	O22 Mn2 O42	91.59(6)
Mn2 O42^{II}	2.210(2)	O2 Mn2 O42	87.71(6)
Mn2 O1	2.264(2)	O12 Mn2 O42^{II}	87.94(6)
		O2 Mn2 O42^{II}	92.60(6)
		O42 Mn2 O42^{II}	80.70(5)
		O12 Mn2 O1	88.86(7)
		O22 Mn2 O1	91.43(5)
		O42 Mn2 O1	85.89(6)
		O42 Mn2 O1^{II}	85.03(5)
FCA (furan-3-carboxylate) 1 ligand			
O11 C11	1.272(2)	C11 O11 Mn1	133.78(12)
O12 C11	1.241(2)	C11 O12 Mn2	128.60(12)
C11 C12	1.453(2)	O12 C11 O11	124.37(15)
C12 C15	1.350(3)	O12 C11 C12	118.48(16)

TABLE V (*Continued*)

	Distance		*Angle*
C12 C13	1.446(3)	O11 C11 C12	117.13(16)
C13 C14	1.284(4)	C15 C12 C13	106.35(19)
C14 O13	1.377(4)	C15 C12 C11	126.20(19)
C15 O13	1.350(3)	C13 C12 C11	127.38(19)
		C14 C13 C12	105.2(2)
		C13 C14 O13	113.3(3)
		O13 C15 C12	110.0(2)
		C15 O13 C14	105.0(2)
FCA 2 ligand			
O21 C21	1.244(2)	C21 O21 Mn1	127.72(12)
O22 C21	1.270(2)	C21 O22 Mn2	134.10(11)
C21 C22	1.469(2)	O21 C21 O22	124.96(15)
C22 C25	1.349(3)	O21 C21 C22	118.58(15)
C22 C23	1.424(3)	O22 C21 C22	116.46(15)
C23 C24	1.357(4)	C25 C22 C23	106.42(19)
C24 O23	1.376(4)	C25 C22 C21	125.97(17)
C25 O23	1.333(3)	C23 C22 C21	127.57(19)
		C24 C23 C22	106.2(2)
		C23 C24 O23	109.21(19)
		O23 C25 C22	110.8(2)
		C25 O23 C24	107.4(2)
FCA 3 ligand			
O31 C31	1.249(2)	C31 O32 Mn1^{I}	123.16(12)
O32 C31	1.268(2)	C31 O32 Mn1	118.90(12)
C31 C32	1.471(3)	Mn1 O32 Mn1^{I}	99.19(5)
C32 C35	1.351(3)	O31 C31 O32	124.41(16)
C32 C33	1.418(3)	O31 C31 C32	118.99(16)
C33 C34	1.346(4)	O32 C31 C32	116.59(17)
C34 O33	1.369(4)	C35 C32 C33	107.24(18)
C35 O33	1.347(3)	C35 C32 C31	125.28(18)
		C33 C32 C31	127.5(2)
		C34 C33 C32	105.6(3)
		C33 C34 O33	110.5(2)
		O33 C35 C32	109.8(2)
		C35 O33 C34	106.9(2)
FCA 4 ligand			
O41 C41	1.244(2)	C41 O42 Mn2	123.35(2)
O42 C41	1.291(2)	C41 O42 Mn2^{II}	118.89(11)
C41 C42	1.440(2)	Mn2 O42 Mn2^{II}	99.30(5)
C42 C45	1.357(3)	O41 C41 O42	123.29(15)
C42 C43	1.439(3)	O41 C41 C42	120.07(16)
C43 C44	1.315(4)	O42 C41 C42	116.63(17)
C44 O43	1.378(4)	C45 C42 C43	105.21(18)
C45 O43	1.345(3)	C45 C42 C41	126.69(17)
		C43 C42 C41	128.1(2)
		C44 C43 C42	106.7(2)
		C43 C44 O43	111.1(2)
		O43 C45 C42	111.0(2)
		C45 O43 C44	105.9(2)

TABLE V (*Continued*)

	Distance $(D-H)$	*Distance* $(H-A)$	*Distance* $(D-A)$	*Angle* $(D-H-A)$
Hydrogen bonds				
O1 H11 O41^{II}	0.982(9)	1.779(10)	2.734(2)	164(2)
O1 H12 O31	0.977(9)	1.752(9)	2.728(2)	177(2)
O2 H21 O22^{III}	0.988(10)	1.797(18)	2.714(2)	153(3)
O2 H22 O41	0.983(10)	2.09(2)	2.826(3)	130(2)
O3 H31 O11^{IV}	0.981(9)	1.772(14)	2.721(2)	162(3)
O3 H32 O31^{I}	0.986(9)	2.08(2)	2.821(2)	131(2)
C14 H14 O33^{V}	0.98	2.51	3.395(4)	158.9
C44 H44 O13^{VII}	0.98	2.47	3.318(3)	151.5
C35 H35 O41^{VII}	0.98	2.46	3.357(3)	162.7
C45 H45 O31	0.98	2.49	3.387(3)	161.7

Symmetry codes: (*I*) $-x, -y, -z+1$; (*II*) $-x, -y+1, -z+1$; (*III*) $1-x, 1-y, 1-z$, (*IV*) $1-x, -y, 1-z$; (*V*) $1+x, 1+y, 1+z$; (*VI*) $x-1, y, z-1$; (*VII*) $x, y-1, z$.

DISCUSSION

Both title compounds exhibit polymeric molecular patterns. The asymmetric unit of manganese thiophenate (title compound I) consists of one manganese cation, two thiophene carboxylate ligands and four water molecules. Three of them are directly bonded to the cation, one is a solvation water. Mn(II) cations are O,O' bridged by thiophencarboxylate groups of one ligand molecule. The second ligand is monodentately bonded to the manganese coordination center, being simultaneously linked to the solvation water molecule *via* a hydrogen bond (see Table IV). In consequence, molecular chains which propagate in the *c*-direction in the crystal are formed. Figure 1 shows a fragment of the chain with numbering of the atoms; Figure 2 illustrates the packing of the chains. The chains are maintained by the hydrogen bond network. Thiophene ring sulfur atoms do not participate in this hydrogen bond network since the closest C–H · · · S contact is 3.46(1) Å. The sulfur atom also shows no bonding interaction with the manganese cation. The coordination around Mn(II) is octahedral. The base of the octahedron consists of the oxygen atom from the bidentate carboxylate group of the bridging ligand [Mn1–O22^{I} 2.134(2) Å], the oxygen atom donated by the monodentate carboxylate group of the second ligand [Mn1–O12 2.158(2) Å] and oxygen atoms of two water molecules [Mn1–O1 2.256(2) Å; Mn1–O2 2.240(2) Å]. The maximum shift from the average plane amounts to 0.047 Å. The vertices of the octahedron are occupied by an oxygen atom (O3) from a water molecule [Mn1–O3 2.226(2) Å] and an oxygen atom (O21) belonging to the bridging carboxylate group of the

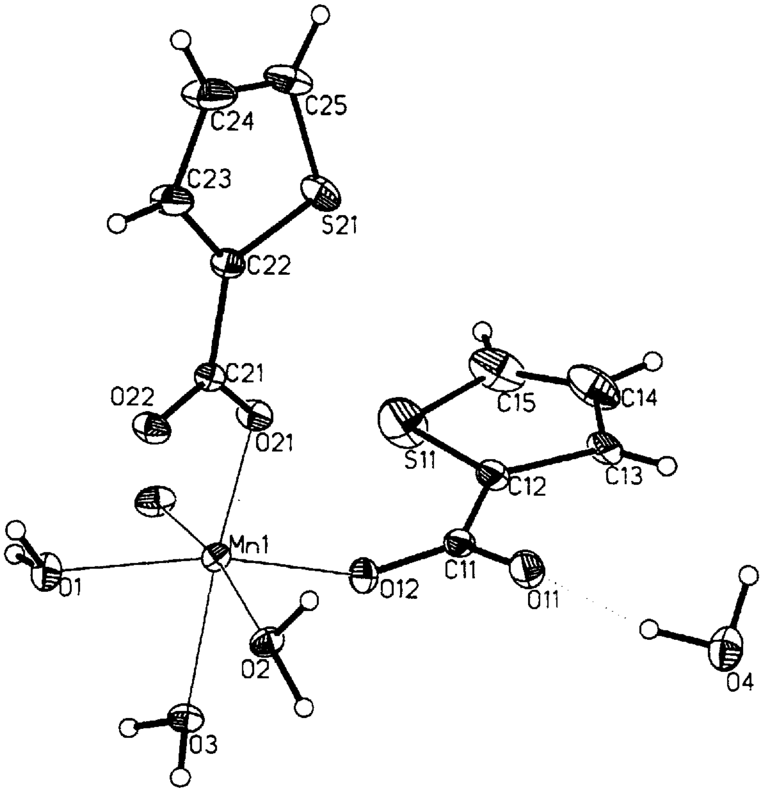

FIGURE 1 The structural unit of $Mn(TCA)_2(H_2O)_3 \cdot (H_2O)$ with numbering of atoms.

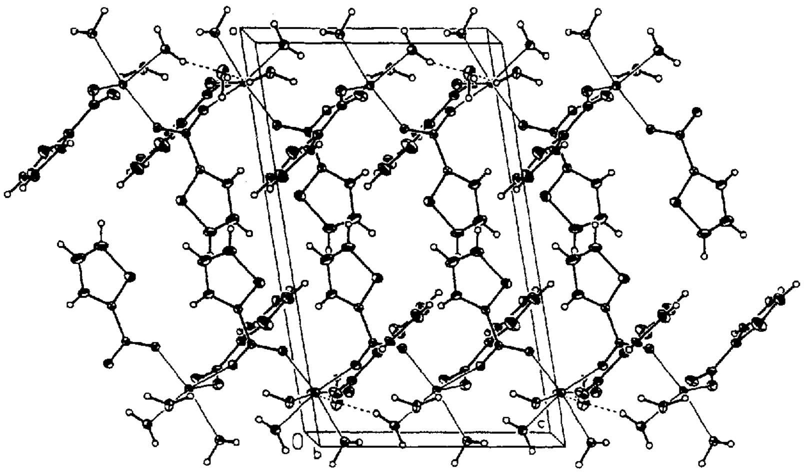

FIGURE 2 The packing diagram of $Mn(TCA)_2(H_2O)_3 \cdot (H_2O)$ viewed along the *c*-axis. Dashed lines indicate the hydrogen bonds.

second ligand [Mn1–O21 2.212(2) Å]. The crystal structure of manganese thiophenate shows close similarity to the structure of magnesium 3-furoate.[7]

Crystals of diaquabis(μ-furan-3-carboxylato-O,O′)tetra(μ-furan-3-carboxylato-O,O)(μ-aqua-O)dimanganese(II) can be described as consisting of dinuclear structural units $Mn_2(FCA)_4(H_2O)_3$, (see Figure 3). Two manganese cations Mn1 and Mn2 inside this unit are bridged by oxygen atoms donated by carboxylic groups of two ligands denoted as FCA1 and FCA2 and an oxygen atom O1 of water molecule situated between the metal ions. In addition, each Mn(II) ion is coordinated by an oxygen atom from a water molecule (O2 and O3, respectively) and oxygen atoms belonging to the carboxylate groups of FCA3 and symmetry related ligands: FCA3^I in the

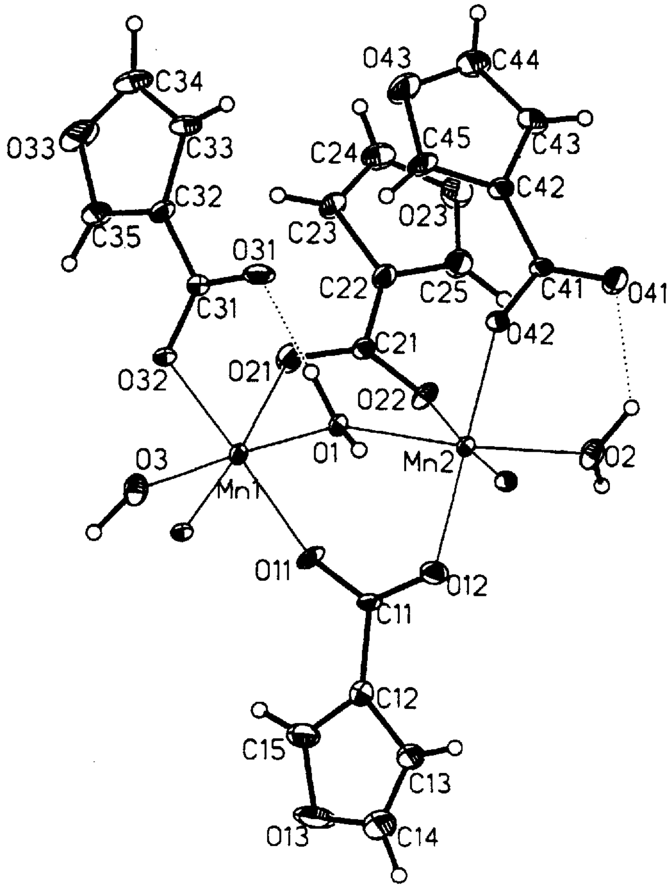

FIGURE 3 The structural unit of $Mn_2(FCA)_4(H_2O)_3$ with numbering of atoms. For the symmetry code see Table V.

case of the Mn1 cation, and FCA4 and FCA4^{I} in the case of the Mn2 cation. O,O′ bridges the Mn1 and Mn2 metal ions in adjacent structural units: O32^{I}–Mn1 2.197(2) Å; O42^{II}–Mn2 2.210(2) Å. Additionally the adjacent monodentate ligands are connected to each other *via* C–H···O hydrogen bonds. Thus the structure of the title compound II is polymeric: molecular ribbons propagate in the *b* direction – see Figure 4. The electron donor ability of the furan ring oxygen atom reveals itself in forming fairly strong C–H···O$_{\text{furan}}$ hydrogen bonds (see Table V) which interconnect the ribbons.

The coordination around each Mn(II) cation in the structural unit is octahedral: the base of the octahedron is formed by two oxygen atoms from the internal bridging bidentate carboxylate groups and by two bridging bidentate oxygen atoms with a mean Mn1–O distance of 2.175 Å and a mean Mn2–O distance of 2.173 Å; the maximal shifts from the average planes are 0.010 and 0.084 Å in the cases of Mn1 and Mn2 containing octahedra, respectively. Both octahedra are slightly elongated along the lines O1–Mn1–O3 and O1–Mn2–O2 since the respective mean bond distances are 2.215 and 2.213 Å. The octahedra are joined by a common apex – the water

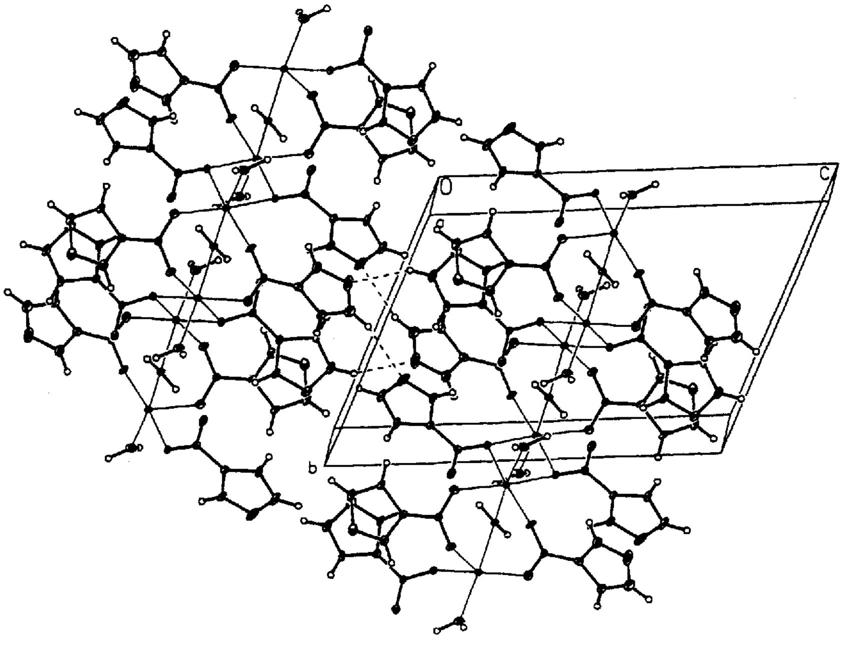

FIGURE 4 The packing diagram of $Mn_2(FCA)_4(H_2O)_3$ viewed along the *b*-axis. Dashed lines indicate the hydrogen bonds.

oxygen atom O1 and are inclined to each other by an angle of 108.0(2)°. One of the features of the molecular patterns observed in both title compounds is the absence of direct bonds between the central ion and the heteroring sulfur atom. Also, the latter does not appear to be an acceptor in the hydrogen bond network. The same effect has been observed in dinuclear complexes of copper(II) with thiophene-2-carboxylate and furan-3-carboxylate ligands[3] as well as in monomeric diaquabis(thiophene-2-carboxylato-*O*)zinc(II) complex.[4]

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