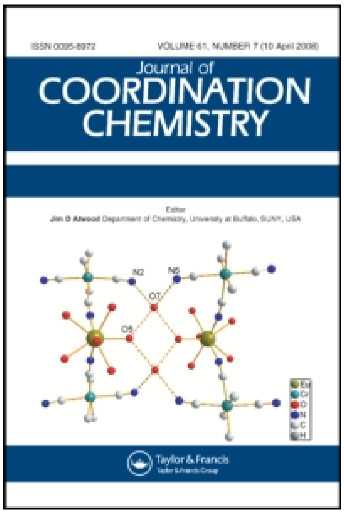

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Synthesis and crystal structure of aqua (2,2'-diamino-4,4'-bi-1,3-thiazole) (oxydiacetato)manganese(II) trihydrate

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SYNTHESIS AND CRYSTAL STRUCTURE OF AQUA (2,2′-DIAMINO-4,4′-BI-1,3-THIAZOLE) (OXYDIACETATO)MANGANESE(II) TRIHYDRATE

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The title compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.194(3)$, $b = 9.790(5)$, $c = 12.492(1)$ Å, $\alpha = 82.407(16)$, $\beta = 86.664(15)$, $\gamma = 89.882(15)^\circ$. The Mn(II) complex assumes distorted octahedral coordination geometry, formed by diaminobithiazole (DABT), an oxydiacetate dianion (ODA) and a water molecule. The tridentate ODA ion chelates to the Mn(II) atom in a *meridional* configuration. Each carboxyl group coordinates to the Mn(II) atom as a monodentate. Uncoordinated carboxyl oxygen atoms are involved in a hydrogen-bonding network. DABT chelates to the Mn(II) atom with a coplanar configuration. Coordinated water is hydrogen bonded to carboxyl groups of ODA of a neighboring complex to form supramolecular chains. A π–π stacking interaction involving thiazole rings occurs between adjacent supramolecular chains. A difference of $180\,\mathrm{cm}^{-1}$ between asymmetric and symmetric stretching vibrations of the carboxyl group corresponds to the extensive hydrogen-bonding network involving the carboxyl group.

Keywords: Manganese(II) complex; Crystal structure; Bithiazole; Aromatic stacking

INTRODUCTION

Transition metal complexes of 2,2′-diamino-4,4′-bi-1,3-thiazole (DABT) or its derivatives have interesting properties and potential applications in many fields. For example, Co(II) and Ni(II) complexes of DABT have been found to be effective inhibitors of DNA synthesis in tumor cells [1,2], and multinuclear Fe(II) and Cu(II) complexes of DABT Schiff bases have been found to be excellent soft magnetic materials [3]. Structural investigation of these complexes is helpful for an understanding of the relationship between properties and structure and for designing new materials. As a part of a series of such investigations the title Mn(II) complex was prepared and its X-ray structure is reported here.

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EXPERIMENTAL

Synthesis

DABT was prepared following the literature method [4]. An aqueous solution (8 cm^3) of DABT (0.10 g, 0.5 mmol) and $MnCl_2 \cdot 4H_2O$ (0.10 g 0.5 mmol) was mixed with an aqueous solution (7 cm^3) containing oxydiacetic acid hydrate (0.076 g, 0.5 mmol), NaOH (0.040 g, 1 mmol) and pyridine (0.08 cm^3). The mixture was refluxed for 3 h and the salmon-pink solution cooled to room temperature and filtered. Single crystals of the title compound were obtained from the filtrate after three days. C, H and N analyses were performed on a Carlo-Erba 1160 instrument. Anal. Calcd. for $[(C_6H_6N_4S_2)(C_4H_4O_5)(H_2O)]Mn \cdot 3H_2O$(%): C, 26.26; N, 12.25; H, 3.94; Found: C, 26.72; N, 12.14; H, 4.11. IR spectra were recorded in KBr pellets in the 4000–400 cm^{-1} region using a Nicolet 5DX FTIR spectrophotometer.

Crystal Structure Determination

X-ray diffraction intensities were collected on a Rigaku AFC-7S diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) using the ω–2θ scan technique at room temperature. The structure was solved by the Patterson method followed by Fourier syntheses. Structure refinement was performed by full-matrix least-squares procedures using SHELXL97 on F^2 [5].

H atoms on water were located in a difference Fourier map and included in final cycles of refinement with fixed positions and a thermal parameter of 0.05 $Å^2$. Other H atoms were placed in calculated positions with C–H = 0.93 Å (aromatic) or 0.97 Å (methylene) and N–H = 0.86 Å, and included in the final cycles of refinement in the riding model, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms.

Crystal data and refinement conditions are summarized in Table I. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in Table II.

TABLE I Crystal data and structure refinement conditions for the title complex

Empirical formula	$C_{10}H_{18}MnN_4O_9S_2$		
Formula weight	457.34		
Crystal size (mm)	0.56 × 0.48 × 0.30		
Temperature (k)	298(2)		
Wavelength (Å)	0.71069		
Crystal system	Triclinic		
Space group	$P\bar{1}$		
Unit cell dimensions (Å,°)	$a = 7.194(3)$	$b = 9.790(5)$	$c = 12.492(1)$
	$\alpha = 82.41(2)$	$\beta = 86.66(2)$	$\gamma = 89.88(2)$
Volume ($Å^3$)	870.6(6)		
Z	2		
Density (calculated) ($g\,cm^{-3}$)	1.745		
Absorption coefficient (mm^{-1})	1.052		
$F(000)$	470		
θ range for data collection (°)	2.1 to 26.0		
Reflections collected	3626		
Independent reflections	3414 ($R_{int} = 0.005$)		
Parameters	247		
Goodness-of-fit on F^2	1.107		
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.029$ $wR2 = 0.084$		
R indices (all data)	$R1 = 0.032$ $wR2 = 0.086$		
Largest diff. peak and hole ($e\,Å^{-3}$)	0.25 and −0.54		

TABLE II Atomic coordinates $[\times 10^4]$ and equivalent isotropic displacement parameters $[\text{Å}^2 \times 10^3]$ of non-H atoms

	x/a	y/b	z/c	U_{eq}
Mn	2865(1)	5116(1)	2445(1)	23(1)
S(1)	4216(1)	863(1)	1084(1)	33(1)
S(1′)	1655(1)	6697(1)	−1247(1)	29(1)
O(1)	4924(2)	6718(2)	2460(1)	33(1)
O(2)	5754(2)	8688(2)	3004(1)	37(1)
O(3)	1467(2)	6922(2)	3102(1)	31(1)
O(4)	178(2)	4431(2)	3251(1)	31(1)
O(5)	−2294(2)	4833(2)	4314(1)	36(1)
O(6)	4084(2)	4133(2)	3986(1)	33(1)
O(7)	9144(3)	9923(2)	1783(2)	54(1)
O(8)	−8(3)	1453(2)	3613(2)	53(1)
O(9)	7485(3)	9624(2)	4812(2)	62(1)
N(2)	4558(3)	1558(2)	3066(2)	40(1)
N(2′)	1322(3)	8042(2)	485(2)	40(1)
N(3)	3518(2)	3231(2)	1700(1)	23(1)
N(3′)	2279(2)	5715(2)	714(1)	23(1)
C(2)	4081(3)	1973(2)	2060(2)	25(1)
C(2′)	1763(3)	6845(2)	119(2)	25(1)
C(4)	3215(3)	3338(2)	600(2)	23(1)
C(4′)	2629(3)	4672(2)	70(2)	22(1)
C(5)	3510(3)	2179(2)	140(2)	32(1)
C(5′)	2378(3)	5015(2)	−993(2)	27(1)
C(11)	4602(3)	7770(2)	2917(2)	26(1)
C(12)	2658(3)	7931(2)	3425(2)	34(1)
C(13)	−268(3)	6698(2)	3716(2)	32(1)
C(14)	−844(3)	5204(2)	3762(2)	25(1)

RESULTS AND DISCUSSION

Crystal Structure

The molecular structure of the title compound is illustrated in Fig. 1. The Mn(II) complex molecule has distorted octahedral coordination geometry (Table III), formed by one DABT ligand, one oxydiacetate dianion and one coordinated water molecule.

The tridentate ligand ODA chelates to an Mn(II) atom in a *meridional* configuration. One of the chelating rings is planar with a maximum atomic deviation of 0.038(1) Å [for atom O(4)]. The other displays an envelope configuration, with atom O(3) at the flap position and 0.293(3) Å out of the mean plane formed by O(1), C(11), C(12) and Mn atoms. Two carboxyl groups of ODA coordinate as monodentates to the Mn(II) atom. The Mn–O(carboxyl) bonds [Mn–O(1) = 2.162(2) and Mn–O(4) = 2.191(2) Å] are significantly shorter than the Mn–O(ether) bond [Mn–O(3) = 2.257(2) Å]. Uncoordinated carboxyl oxygen atoms [O(2) and O(5)] are hydrogen bonded to lattice water and coordinated water of a neighboring complex molecule, as shown in Fig. 1 and Table IV.

DABT chelates to the Mn(II) atom with a coplanar configuration, the maximum atomic deviation being 0.052(2) Å [C(5′)]. This is different from the twisted structures of thiazole found in a Cd(II) complex [6] and an Ni(II) complex [7], but comparable to that found in a Cu(II) complex [8]. Essentially identical C–N bond distances [C(2)–N(2) = 1.332(3) and C(2)–N(3) = 1.325(3) Å; C(2′)–N(2′) = 1.343(3) and C(2′)–N(3′) = 1.315(3) Å] suggest electron delocalization between the amino groups and the

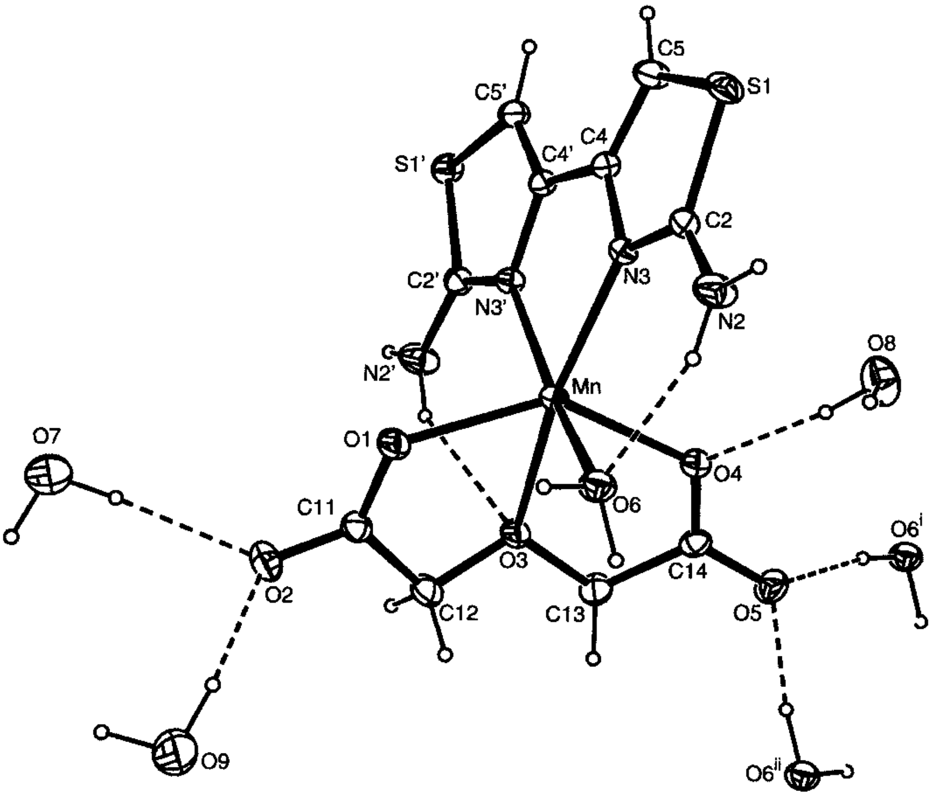

FIGURE 1 The molecular structure of the title complex with 30% probability displacement ellipsoids; dashed lines show hydrogen bonding. [Symmetry codes: (i) −1 + x, y, z; (ii) −x, 1 − y, 1 − z].

TABLE III Selected bond lengths and angles [Å,°]

Mn–O(1)	2.162(2)	Mn–O(3)	2.257(2)
Mn–O(4)	2.191(2)	Mn–O(6)	2.260(2)
Mn–N(3)	2.212(2)	Mn–N(3′)	2.228(2)
S(1)–C(2)	1.737(2)	S(1′)–C(2′)	1.737(2)
S(1)–C(5)	1.724(2)	S(1′)–C(5′)	1.721(2)
O(1)–C(11)	1.257(3)	O(2)–C(11)	1.243(3)
O(3)–C(12)	1.421(3)	O(3)–C(13)	1.428(3)
O(4)–C(14)	1.262(3)	O(5)–C(14)	1.244(3)
N(2)–C(2)	1.333(3)	N(2′)–C(2′)	1.344(3)
N(3)–C(2)	1.324(3)	N(3′)–C(2′)	1.315(3)
N(3)–C(4)	1.394(3)	N(3′)–C(4′)	1.395(2)
C(4)–C(4′)	1.457(3)	C(4)–C(5)	1.349(3)
C(4′)–C(5′)	1.349(3)	C(11)–C(12)	1.518(3)
C(13)–C(14)	1.514(3)		
O(1)–Mn–O(3)	71.53(6)	O(1)–Mn–O(4)	139.70(6)
O(1)–Mn–O(6)	85.44(7)	O(1)–Mn–N(3)	121.50(6)
O(1)–Mn–N(3′)	94.51(6)	O(3)–Mn–O(4)	71.25(6)
O(3)–Mn–O(6)	98.14(6)	O(3)–Mn–N(3)	165.64(6)
O(3)–Mn–N(3′)	97.45(6)	O(4)–Mn–O(6)	85.02(6)
O(4)–Mn–N(3)	97.47(6)	O(4)–Mn–N(3′)	105.06(6)
O(6)–Mn–N(3)	89.45(6)	O(6)–Mn–N(3′)	163.53(6)
N(3)–Mn–N(3′)	76.50(6)		

TABLE IV Hydrogen-bonding geometry [Å,°]

$D–H\cdots A$	$d(D–H)$	$d(H\cdots A)$	$d(D\cdot A)$	(DHA)
N(2)–H(21)···O(6)	0.86	2.13	2.917(3)	152
N(2)–H(22)···O(2)[a]	0.86	2.14	2.947(3)	157
N(2′)–H(21′)···O(3)	0.86	2.55	3.315(3)	149
N(2′)–H(22′)···O(7)[b]	0.86	2.48	3.275(3)	153
O(6)–H(61)···O(5)[c]	0.89	1.88	2.763(3)	170
O(6)–H(62)···O(5)[d]	0.96	1.78	2.726(3)	171
O(7)–H(71)···O(2)	0.92	2.07	2.971(3)	165
O(7)–H(72)···O(8)[e]	0.92	2.08	2.986(3)	168
O(8)–H(81)···O(4)	0.91	1.99	2.893(3)	172
O(8)–H(82)···O(9)[f]	0.95	1.95	2.853(3)	159
O(9)–H(91)···O(2)	0.99	1.92	2.893(3)	169
O(9)–H(92)···O(8)[e]	0.99	1.82	2.773(4)	160

Symmetry codes: (a) $x, -1+y, z$; (b) $1-x, 2-y, -z$; (c) $1+x, y, z$; (d) $-x, 1-y, 1-z$; (e) $1+x, 1+y, z$; (f) $1-x, 1-y, 1-z$.

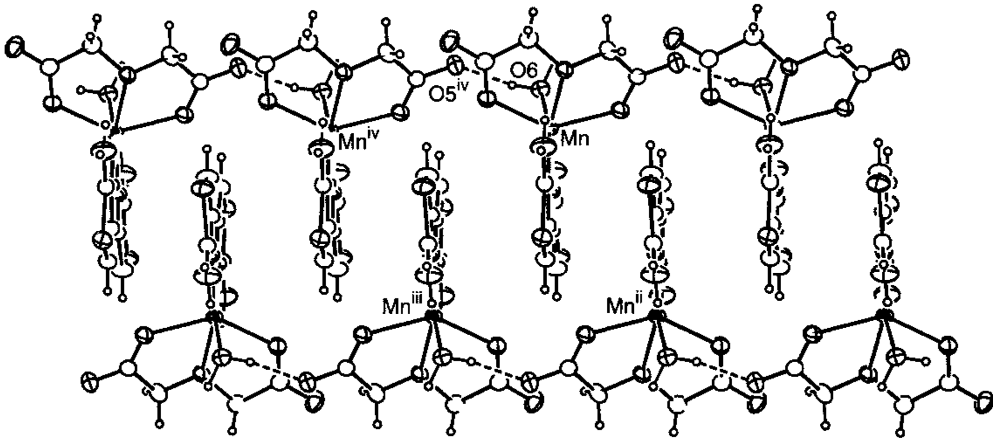

FIGURE 2 Diagram showing the overlapped arrangement of DABT ligands from adjacent hydrogen-bonded supramolecular chains. [Symmetry codes: (ii) $-x, 1-y, -z$; (iii) $1-x, 1-y, -z$; (iv) $1+x, y, z$].

thiazole ring. The amino groups are hydrogen bonded to coordinated ether oxygen [O(3)] or coordinated water [O(6)] (Fig. 1 and Table IV) to stabilize the molecular structure.

It is notable that the O(1)–Mn–N(3) bond angle [121.50(6)°] is much larger than O(4)–Mn–N(3) [97.47(6)°], but Mn–O(1) [2.162(2) Å] and Mn–N(3) [2.212(2) Å] bond distances are appreciably shorter than corresponding Mn–O(4) [2.191(2) Å] and Mn–N(3′) [2.228(2) Å] bonds, respectively. This fact may imply a more electrostatic interaction in coordination of the Mn(II) complex [9].

A water molecule [O(6)] coordinates to the Mn(II) atom to complete the distorted octahedral coordination geometry. The coordinated water is hydrogen bonded to the carboxyl group of a neighboring complex molecule to form a supramolecular chain (Fig. 2) along the *a* axis.

The parallel arrangement of thiazole rings from adjacent hydrogen-bonded supramolecular chains, related by an inversion center, is observed (Fig. 2). The separations between neighboring parallel thiazole rings, 3.336(6) Å ($-x$, $1-y$, $-z$) and 3.441(6) Å ($1-x$, $1-y$, $-z$), clearly suggests the existence of the π–π stacking.

Infrared Spectrum

Infrared spectra of the compound and H_2ODA were recorded for comparison. Stretching of the C–O–C bond is observed at $1100\,cm^{-1}$ in both complex and H_2ODA, the relatively weaker absorption in the complex corresponding to coordination of the ether oxygen atom. Symmetric and asymmetric stretching vibrations of the carboxyl group are observed at 1420 and $1600\,cm^{-1}$, respectively. The difference of $180\,cm^{-1}$ is smaller than the expected value of $200\,cm^{-1}$ for a monodentate carboxyl group [10] and may be due to the extensive hydrogen-bonding network involving carboxyl groups as mentioned above.

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Supplementary Data

Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with deposition number CCDC 230117.

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