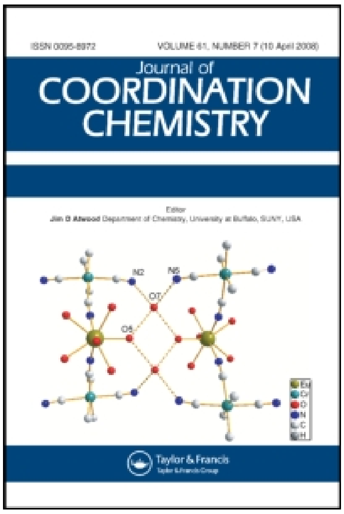

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SYNTHESIS AND CRYSTAL STRUCTURE OF TETRAIMIDAZOLE(DIAQUA)-MANGANESE(II) TEREPHTHALATE

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The title complex, $[Mn(C_3H_4N_2)_4(H_2O)_2]\cdot(C_8H_4O_4)$, was prepared by reaction of terephthalato (diaqua)manganese (II) with imidazole in ethanol/water solution. The complex crystallizes in space group *C2/c* with cell parameters $a = 22.494(5)$, $b = 7.741(2)$, $c = 16.287(3)$ Å, $\beta = 120.92(3)°$, $Z = 4$. The complex consists of complex Mn(II) cations and uncoordinated terephthalate anions; the latter link cations through an H-bonding network. Thermal analyses and IR spectra are discussed in terms of the formation of the complex.

Keywords: Manganese(II); Synthesis; Crystal structure; Terephthalate; Thermal analysis; IR

INTRODUCTION

As coordination of water molecules to the manganese atom is an important step for oxygen evolution in the photosynthesis process, many multinuclear manganese complexes with coordinated water molecules have been investigated as model compounds for oxygen evolution [1]. We have been interested in the structural chemistry of multinuclear manganese complexes with coordinated water for several years and a series of manganese complexes bridged by the carboxyl group has been synthesized in our laboratory [2]. X-ray structure analyses of these complexes showed a variety of coordination modes for the carboxyl group. Recently we tried to prepare a Mn(II)

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*Corresponding author.

complex bridged by the terephthalate group, but X-ray diffraction analysis revealed an unexpected structure consisting of uncoordinated terephthalate anions and complex Mn(II) cations. We present here the crystal structure and discuss the possible reasons for forming the ionic compound.

EXPERIMENTAL

Synthesis

Some 5 mmol (0.83 g) of terephthalic acid was slowly added to an aqueous solution of NaOH (0.40 g, 10 mmol, 10 cm^3) with stirring at room temperature. When 10 cm^3 of an aqueous solution containing 5 mmol of $MnCl_2$ was dropped into the above solution, a white precipitate was obtained immediately. The precipitate was separated from the solution. Elemental analysis and infrared spectra suggested it to be terephthalato-(diaqua)manganese(II) (complex 1), as mentioned below. Complex 1 is insoluble in most solvents and barely dissolves in hot ethanol/water. After separating the precipitate, a saturated solution of complex 1 was obtained. Into this solution, an ethanol solution (20 cm^3) containing 10 mmol of imidazole was added at room temperature. The reaction mixture was left to stand for several days until colourless single crystals of the title complex (complex 2) were obtained.

Physical Measurements

Complexes 1 and 2 were analyzed using a Carlo-Erba 1160 instrument *Anal.* Calc. for $Mn(H_2O)_2C_8H_4O_4$ (complex 1) (%): C, 37.66; H, 3.14. Found: C, 37.65; H, 3.29. Calc. for $Mn(C_3H_4N_2)_4(H_2O)_2 \cdot C_8H_4O_4$ (complex 2): C, 45.55; N, 21.25; H, 4.55. Found: C, 44.83; N, 22.21; H, 4.76. IR spectra of both complexes were recorded with a Shimadzu IR-470 spectrophotometer (4000–400 cm^{-1}) using a powdered sample spread on KBr plates. Thermal analyses of both complexes to 650°C were obtained using a Delta TGA7 thermogravimetric balance.

Crystal Structure Determination

X-ray diffraction intensity data were collected on a Rigaku AFC7R diffractometer up to a 2θ value of 55.0° with graphite-monochromatized

TABLE I Atomic coordinates [Å × 10^4] and equivalent isotropic displacement parameters [$Å^2$ × 10^3] for the non-hydrogen atoms. $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	$U(eq)$
Mn	2500	2500	0	30(1)
O(1W)	2393(1)	5236(2)	−467(1)	39(1)
O(1)	1567(1)	−2752(2)	−122(1)	38(1)
O(2)	673(1)	−2943(2)	84(1)	48(1)
N(1)	2159(1)	1695(2)	−1510(1)	37(1)
N(2)	1392(1)	2362(2)	−375(1)	37(1)
N(3)	1602(1)	1819(3)	−3076(1)	47(1)
N(4)	438(1)	2496(3)	−324(2)	48(1)
C(1)	2246(1)	170(3)	−1861(2)	51(1)
C(2)	1906(1)	245(4)	−2826(2)	61(1)
C(3)	1766(1)	2644(3)	−2270(2)	44(1)
C(4)	1094(1)	2989(3)	77(2)	43(1)
C(5)	297(1)	1484(4)	−1081(2)	65(1)
C(6)	883(1)	1395(4)	−1103(2)	57(1)
C(7)	932(1)	−2915(3)	−438(1)	33(1)
C(8)	448(1)	−3067(3)	−1507(1)	32(1)
C(9)	705(1)	−3080(4)	−2115(1)	46(1)
C(10)	−261(1)	−3094(4)	−1904(1)	49(1)

MoKα radiation ($\lambda = 0.71073$ Å) using the $\omega - 2\theta$ scan technique. Among the 2477 reflections collected, 2130 reflections were considered as observed [$I > 2\sigma(I)$] and used for the structure determination. Usual Lp and empirical adsorption corrections were applied. The structure was solved by the Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the SHELX93 program package [3]. H atom sites were obtained from a difference Fourier map and fixed during structure refinement. Final anisotropic refinement including all non-H atoms converged to agreement factors $R = 0.0348$ and $R_w = 0.0435$, where $w = 1/[\sigma^2(F) + 0.004458\ F^*F]$. Atomic scattering factors were taken from International Tables for X-ray Crystallography [4]. Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in Table I.

Crystal Data

$Mn(C_3H_4N_2)_4(H_2O)_2 \cdot C_8H_4O_4$, $M = 527.4$, monoclinic, $C2/c$, $a = 22.494(5)$, $b = 7.741(2)$, $c = 16.287(3)$ Å, $\beta = 120.92(3)°$, $V = 2432.8(8)$ Å^3, $Z = 4$, $F(000) = 1092$, $D_c = 1.44\ \mathrm{g \cdot cm^{-3}}$, $\mu(\mathrm{MoK}\alpha) = 0.59\ \mathrm{mm^{-1}}$, $S = 1.043$, $(\Delta\rho)_{max} = 0.400$, $(\Delta\rho)_{min} = -0.378\ \mathrm{e \cdot Å^{-3}}$.

RESULTS AND DISCUSSION

Crystal Structure

The molecular structure of the title complex is illustrated in Figure 1 with the atom numbering scheme. Selected bond distances and angles, together with atomic separations involved in the H-bond network, are listed in Table II.

The complex consists of complex Mn(II) cations and terephthalate anions. The Mn(II) atom located on an inversion centre exhibits octahedral coordination geometry. Four imidazole and two water molecules coordinate to the Mn(II) atom with normal bond distances and angles. The Mn–O(1W) distance of 2.221(2) Å is comparable to 2.221(6) Å in $[Mn(HC_4O_4)_2(H_2O)_4]$ [5]. The Mn–N distances of 2.244(2) and 2.255(2) Å are a little longer than

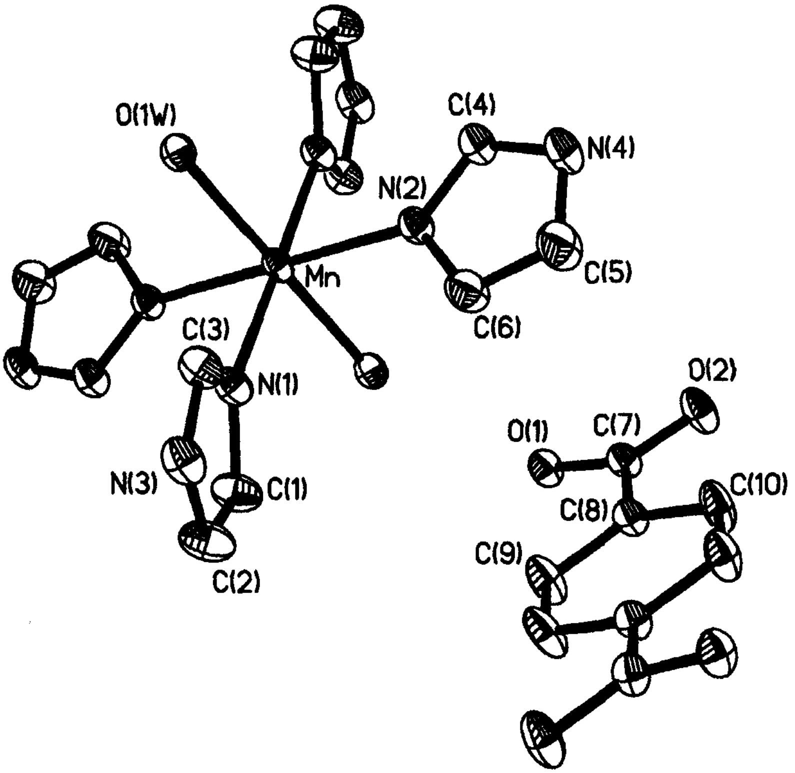

FIGURE 1 The molecular structure of title complex showing 30% probability displacement ellipsoids. H atoms are omitted for clarity.

TABLE II Selected bond distances [Å] and angles [°]

Mn–O(1W)	2.221(2)	Mn–N(1)	2.255(2)
Mn–N(2)	2.244(2)	O(1)–C(7)	1.252(2)
O(2)–C(7)	1.254(2)	N(1)–C(3)	1.315(3)
N(1)–C(1)	1.369(3)	N(2)–C(4)	1.314(3)
N(2)–C(6)	1.372(3)	N(3)–C(3)	1.330(3)
N(3)–C(2)	1.354(4)	N(4)–C(4)	1.326(3)
N(4)–C(5)	1.354(3)	C(1)–C(2)	1.351(3)
C(5)–C(6)	1.337(4)		
O(1)–O(1W)[a]	2.695(2)	O(1)–O(1W)[b]	2.807(2)
O(2)–N(3)[c]	2.770(2)	O(2)–N(4)[d]	2.743(2)
O(1W)–Mn–N(1)	88.48(6)	O(1W)–Mn–N(2)	92.43(6)
N(1)–Mn–N(2)	88.99(7)	O(1)–C(7)–O(2)	123.6(2)
O(1)–C(7)–C(8)	118.5(2)	O(2)–C(7)–C(8)	117.9(2)

Symmetry codes: [a] $x, -1+y, z$.
[b] $0.5-x, 0.5-y, 0.5-z$.
[c] $x, -y, 0.5+z$.
[d] $-x, -y, -z$.

2.228(2) and 2.236(9) Å in $[Mn_2(C_{10}H_2O_8)(C_3H_4N_2)_6(H_2O)_4] \cdot 4H_2O$ [6]. The terephthalate anion located around another inversion centre does not coordinate to the Mn(II) atom but links the complex cations through an extensive H-bonding network. The carboxyl O(1) atom links two coordinated water molecules while the carboxyl O(2) atom links two coordinated imidazole molecules. Several transitional metal complexes of terephthalate have been synthesized and their X-ray structures show different coordination modes for the terephthalate group (monodentate, chelating, bridging *etc.*) [7]. To our knowledge, no uncoordinated terephthalate anion has been found in transitional metal complexes.

Infrared Spectra

Carboxyl group stretching was observed at 1389 cm^{-1} [ν_s(COO)] and 1549 cm^{-1} [ν_{as}(COO)] for complex 1, and at 1382 cm^{-1} [ν_s(COO)] and 1565 cm^{-1} [ν_{as}(COO)] for complex 2. Compared with the uncoordinated carboxyl group in complex 2, the asymmetric stretch of complex 1 shifts by some 16 cm^{-1} to lower frequency. The $\Delta\nu$ value of 160 cm^{-1} implies that each carboxyl group *u*-bridges two Mn(II) atoms in complex 1 [8].

Thermal Analysis

For complex 1, 15.44% weight was lost between 130 and 155°C, and 56.29% between 250 and 545°C. For complex 2, 7.04% was lost between 105 and 115°C, 50.81% between 215 and 370°C and 24.11% between 370 and 560°C.

For complex 2, $[Mn(C_3H_5N_2)_4(H_2O)_2 \cdot C_8H_4O_4]$, the three stages correspond to the loss of two water molecules (Calc. 6.83%), four imidazole molecules (Calc. 51.61%) and oxidation of terephthalate and Mn element (Calc. 25.05% if final residue is MnO_2), respectively. The results agree well with the crystal structure.

For complex 1, the two stages of weight loss correspond to the loss of two water molecules and oxidation of terephthalate and Mn, respectively, and suggest the formula $Mn(C_8H_4O_4)(H_2O)_2$ with calculated weight losses of 14.12 and 58.04% (if the final residue is MnO).

Combining the above data, we propose that complex 1 possesses an infinite polymeric network structure in the solid state, in which each terephthalate group bridges four Mn(II) atoms through both carboxyl groups.

Synthesis

As discussed above, the polymeric complex 1 was obtained in the reaction of terephthalate and $MnCl_2$. It is easy to accept the low solubility of the complex, as the polymer must be decomposed in order to dissolve. Decomposition of the complex probably results in mainly uncoordinated terephthalate anions and hydrated Mn(II) cations. Imidazole is clearly a stronger ligand towards Mn(II) than either terephthalate or water, and thus complex 2 was simply obtained.

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

Acknowledgement

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