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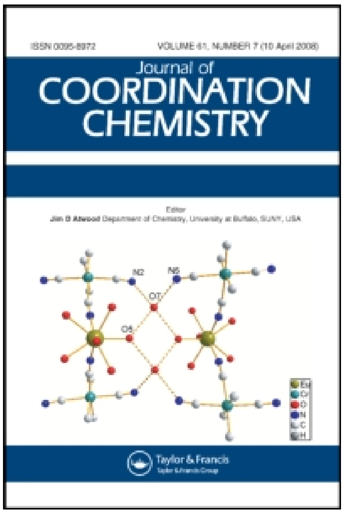

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Synthesis and Crystal Structure of BIS(Imidazole)(μ-Succinato) Manganese(II)

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Note

SYNTHESIS AND CRYSTAL STRUCTURE OF BIS(IMIDAZOLE)(μ-SUCCINATO) MANGANESE(II)

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The title complex was prepared by reaction of succinatomanganese(II) with imidazole in water–ethanol. The complex crystallizes in orthorhombic space group $Pna2_1$ with $a = 7.9990(15)$, $b = 14.8690(15)$, $c = 11.028(2)$ Å. The metal assumes a distorted octahedral coordination. In the crystal, each succinate dianion bridges three Mn(II) atoms to form a polymer with a layered structure.

Keywords: Crystal structure; Manganese; Imidazole; Succinic acid

INTRODUCTION

As model compounds of the active centre on photosystem II, multinuclear manganese complexes have attracted much interest. A series of manganese complexes bridged by dicarboxylate has been synthesized in their crystal structures show versatile coordination modes by the carboxyl group [1,2]. Recently we prepared a manganese(II) complex bridged by succinate. X-ray diffraction analysis showed the existence of different coordination modes of the succinate dianion in the polymeric complex.

EXPERIMENTAL

Preparation

$MnCO_3$ (0.92 g, 8 mmol) was added to a hot aqueous solution (20 cm^3) containing succinic acid (0.95 g, 8 mmol); the solution was heated at 60°C with stirring until no more CO_2 was released. An ethanol solution (10 cm^3) of imidazole (0.68 g, 10 mmol) was slowly added to the above solution and the mixture refluxed for 45 min and

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filtered. Colourless crystals were obtained from the filtrate after 3 weeks. *Anal.* cald. for $C_{10}H_{12}N_4O_4Mn$ (%): C, 39.07; H, 3.91; N, 18.23; found: C, 38.88; H, 3.62; N, 18.54. The IR of the complex was recorded with a Shimadzu IR-470 spectrophotometer (4000–400 cm^{-1}) using a powdered sample spread on a KBr plate.

Crystal Structure Determination

A prismatic crystal of approximate dimensions of 0.64 × 0.40 × 0.28 mm was mounted on a glass fibre. Intensity data were collected on a Rigaku AFC7S diffractometer up to a 2θ value of 50.0° with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) using the $\omega - 2\theta$ technique. A total of 1213 independent reflections was collected, of which 1088 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-square procedures using the SHELX program package [3]. A disordered succinate group was observed as mentioned below. H atoms, except those bonding to disordered carbon atoms, were located in a difference Fourier map and fixed during structure refinement. Anisotropic refinement including all non-H atoms converged to agreement factors $R = 0.024$ and $R_w = 0.072$ where $w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.3489P]$ and $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors were taken from International Tables for X-ray Crystallography [4]. Systematic absences suggests that another possible space group is *Pnma*, but this choice failed to give satisfactory structure.

Crystal data

$C_{10}H_{12}N_4O_4Mn$, $Mr = 307.18$, Orthorhombic, $Pna2_1$, $a = 7.9990(15)$, $b = 14.8690(15)$, $c = 11.028(2)$ Å, $V = 1311.6(3)$ Å^3, $z = 4$, $F(000) = 628$, $D_c = 1.556$ g cm^{-3}, μ(Mo$K\alpha$) = 1.022 mm^{-1}, $S = 1.131$, $(\Delta\rho)_{\max} = 0.27$, $(\Delta\rho)_{\min} = -0.29$ eÅ^{-3}.

RESULTS AND DISCUSSION

Final fractional atomic coordinates for non-hydrogen atoms are listed in Table I. The molecular structure is illustrated in Fig. 1. Two nitrogen atoms of imidazole molecules and one carboxyl group of a succinate form an equatorial plane around a Mn(II) atom; two oxygen atoms from other succinate dianions occupy apical positions to complete a distorted octahedral coordination around the Mn(II) atom.

The N(1)–Mn–N(3) bond angle of 118.7° is much larger than the expected value of 90°, suggesting non-ideal overlap between the atomic orbitals of Mn(II) and the donor nitrogen atoms. However, the Mn–N(1) distance 2.183(3) and Mn–N(3) distance 2.190(3) Å are significantly shorter than those found in a tetraimidazole complex of Mn(II) [5], in which perpendicular Mn–N (imidazole) bonds imply maximum overlap of atomic orbitals. This strongly suggests significant electrostatic interaction between Mn(II) and imidazole in the complex. Bond angles Mn–O(1)–C(1) [136.8(3)°] and Mn–O(2C)–C(1C) [138.2(3)°] seriously deviate from the expected value of 120°. However both the Mn–O(1) distance [2.117(3) Å] and Mn–O(2C)

TABLE I Atomic fractional coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) of non-H atoms

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
Mn	662(1)	15(1)	−2(1)	23(1)
O(1)	2113(3)	−29(2)	−1607(3)	47(1)
O(2)	426(3)	−54(1)	−3191(3)	34(1)
O(3)	7257(3)	789(1)	−4092(2)	36(1)
O(4)	6936(3)	−661(1)	−4093(2)	38(1)
N(1)	−470(3)	1316(2)	−412(3)	34(1)
N(2)	−1202(4)	2726(2)	−183(4)	50(1)
N(3)	−749(3)	−1210(2)	−411(3)	35(1)
N(4)	−1619(4)	−2593(2)	−156(4)	53(1)
C(1)	1842(4)	−80(2)	−2720(3)	32(1)
C(2A)*	3372(8)	−369(5)	−3488(7)	28(2)
C(2B)*	3358(11)	−19(5)	−3574(9)	33(2)
C(3A)*	4728(14)	368(6)	−3321(10)	39(3)
C(3B)*	4973(16)	108(11)	−2868(12)	71(5)
C(4)	6431(5)	108(2)	−3823(4)	35(1)
C(5)	−451(4)	2028(2)	311(4)	44(1)
C(6)	−1725(5)	2475(3)	−1296(4)	54(1)
C(7)	−1272(4)	1601(2)	−1434(3)	40(1)
C(8)	−804(4)	−1910(3)	324(4)	45(1)
C(9)	−2131(6)	−2338(3)	−1268(4)	62(1)
C(10)	−1577(4)	−1485(2)	−1423(4)	46(1)

*Atoms with 0.5 site occupancy factor.

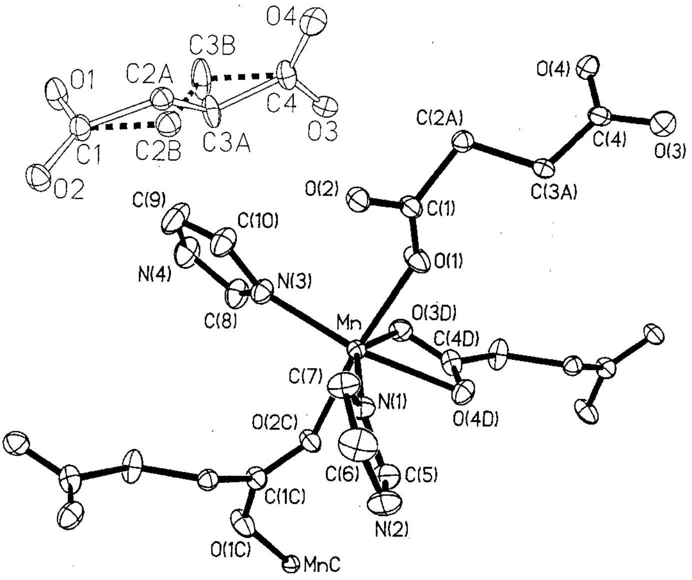

FIGURE 1 Molecular structure showing 30% probability displacement ellipsoids. A disordered succinate group is illustrated at the upper-left of the figure.

distance [2.180(3) Å] are normal. This suggests the existence of electrostatic interaction between Mn(II) and donor oxygen atoms.

A disordered succinate dianion was observed during the structure refinement. While both carboxyl groups coordinate normally to Mn(II) atoms, C(2) and C(3) atoms display a disordered distribution as shown in Fig. 1, with each disordered position A and B having 0.5 site occupancy. The disordered fragment has reasonable bond distances and angles.

Each succinate dianion briges three Mn(II) atoms to form a polymeric complex. Carboxyl groups of the succinate dianion display different coordination modes; one chelates a Mn(II) and another bridges two other Mn(II) atoms. The polymeric complex possesses a layered structure as shown in Fig. 2. All Mn(II) atoms of a polymeric molecule are coplanar and imidazole molecules locate on both sides of the Mn plane. H-bonding between imidazole and carboxyl groups of adjacent layers form a three-dimensional supra-molecular structure. In the IR peaks at 1395 and 1465 cm^{-1} are assigned to the asymmetrical and symmetrical stretching vibration of the carboxyl group chelating a Mn(II) atom, while peaks at 1410 and 1555 cm^{-1} are assigned to the asymmetrical and symmetrical stretching vibration of the carboxyl group bridging two Mn(II) atoms. Differences in frequencies of 70 and 145 cm^{-1} agree with those reported for other chelating and bridging carboxyl groups [6].

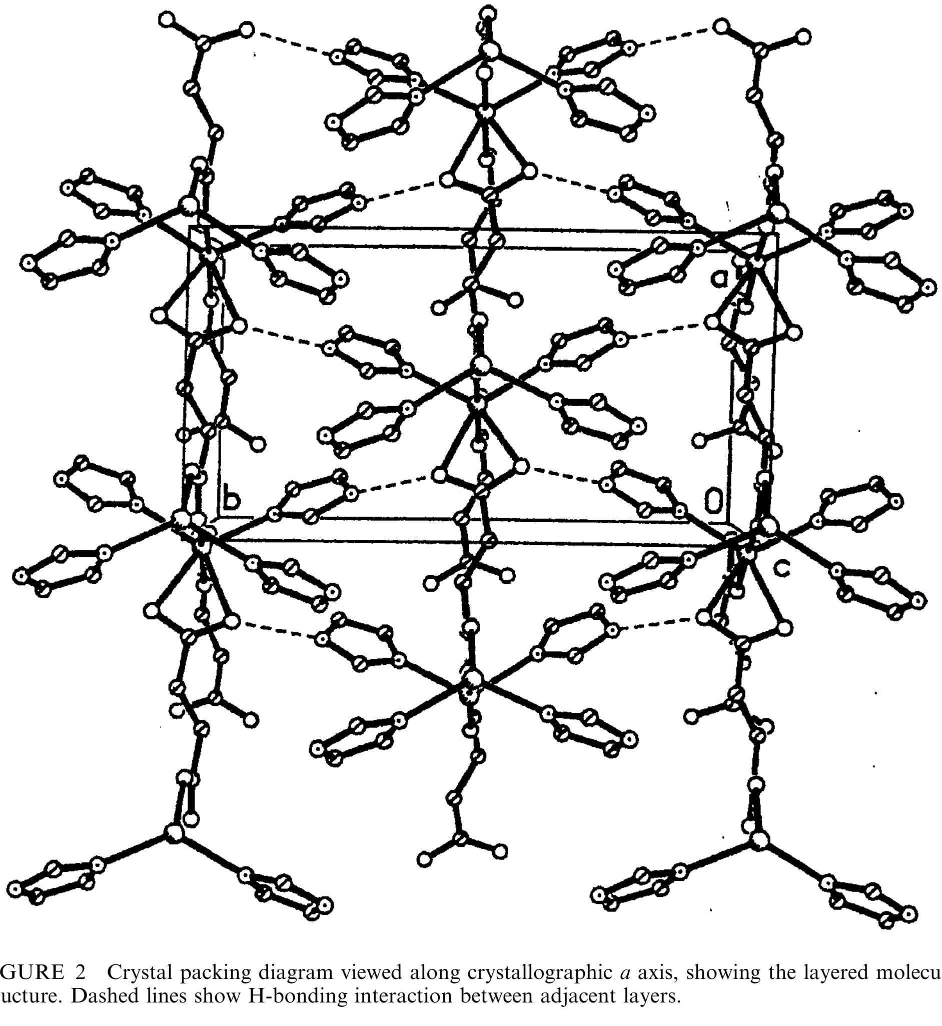

FIGURE 2 Crystal packing diagram viewed along crystallographic *a* axis, showing the layered molecular structure. Dashed lines show H-bonding interaction between adjacent layers.

Acknowledgements

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Supplementary Material

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

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