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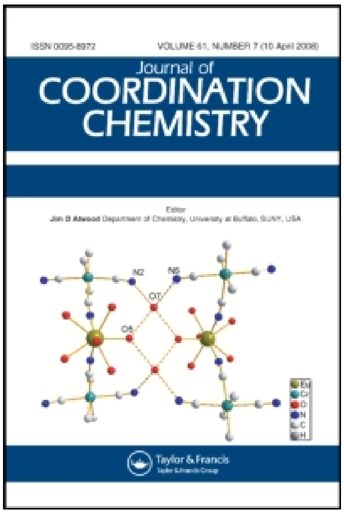

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Synthesis and Crystal Structure of an Mn(II) Complex with Benzoylacetone

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SYNTHESIS AND CRYSTAL STRUCTURE OF AN Mn(II) COMPLEX WITH BENZOYLACETONE

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The complex (benzoato)benzoylacetonato(bipyridine)Mn(II) has been prepared and its crystal structure determined by X-ray diffraction methods. Benzoic acid, benzoylacetone (bzac) and 2,2′-bipyridine all chelate to Mn(II) to form a six coordinate complex. As bond angles around the Mn(II) atom greatly deviate from those expected for an octahedron, the coordination geometry may be described as distorted pyramidal with a bidentate carboxyl group occupying the apex of the pyramid. Although the Mn atom deviates by 0.550 Å from the enol ring plane of bzac, Mn–O distances [2.105(2) and 2.098(2) Å] are normal. This suggests the existence of electrostatic interactions between Mn(II) and the bzac ligand.

Keywords: Manganese(II) complex; Benzoylacetone; Crystal structure; Electrostatic interactions

INTRODUCTION

Recently, intense efforts have attended the nature of the biological unit responsible for water oxidation in the photosynthetic apparatus of green plants [1]. The process of water splitting is generally believed to occur at a manganese cluster located in the reaction centre of photosystem II [2]. In order to mimic the manganese cluster, a series of manganese complexes have been synthesized and their crystal structures have been determined [3–11]. Several structures showed evidence for the existence of electrostatic interactions between Mn(II) and the ligand [7,9], which is considered to be an important factor for oxygen release during photosynthesis [12]. As a part of this research a new Mn(II) complex with benzoylacetone (bzac) has been prepared. The structure of the complex also shows the existence of electrostatic interactions between Mn(II) and the bzac ligand.

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EXPERIMENTAL

Synthesis

An aqueous solution (10 cm^3) containing benzoic acid (5 mmol) and NaOH (5 mmol) was slowly added to an aqueous solution (10 cm^3) containing $MnCl_2$ (5 mmol) with stirring at room temperature. A great deal of precipitate immediately appeared, which was separated from the aqueous solution and dissolved in ethanol (10 cm^3). To the ethanol solution another ethanol solution (15 cm^3) containing 2,2′-bipyridine (5 mmol) and benzoylacetone (5 mmol) was slowly added with continuous stirring. The mixture was refluxed for 20 min, then cooled to room temperature and filtered. Brown-red single crystals were obtained from the filtrate after two weeks.

Physical Measurements

C, N and H contents were analyzed using a Carlo-Erba 1160 instrument. *Anal.* Calc. for $C_{27}H_{22}MnN_2O_4 \cdot 0.5H_2O$(%): C, 64.49; N, 5.57; H, 4.61; Found: C, 64.54; N, 5.35; H, 5.03. The IR spectrum of the title complex was measured in KBr discs using a Nicolet 5DX FT-IR spectrophotometer.

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Crystal Structure Determination

A prismatic, single crystal with approximate dimensions 0.30 × 0.20 × 0.22 mm was mounted on a glass fibre. X-ray diffraction intensity data were collected at 298 K on a Rigaku AFC-7R diffractometer up to $2\theta_{max}$ of 50° with graphite-monochromated MoKα radiation. A total of 4220 reflections were collected, of which 2917 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 direct methods followed by Fourier syntheses. The O(5) atom of crystalline water was located at a position close to a crystallographic inversion centre and its site occupation factor converged to 0.48 during refinement. The site factor of this disordered O(5) atom was fixed as 0.5 during final cycles of structure refinement. Structure refinement was carried out with full-matrix least-squares procedures using the SHELXL-97 programme package [13]. H atoms on phenyl rings were placed at calculated positions with C–H distances of 0.93 Å and riding on carrier atoms. H atoms of the disordered O(5) atom were not located. Other H atoms were located in a difference Fourier map and not refined. Anisotropic refinement including all non-H atoms converged to $R = 0.034$ for all observed reflections. Final fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Table I.

Crystal Data

$C_{27}H_{22}MnN_2O_4 \cdot O.5H_2O$, $M = 502.41$, triclinic, space group $P\bar{1}$, $a = 11.133(2)$, $b = 12.208(2)$, $c = 9.281(2)$ Å, $\alpha = 102.12(3)$, $\beta = 102.32(3)$, $\gamma = 83.56(3)°$, $V = 1201.9(4)$ Å^3, $Z = 2$, $F(000) = 520$, $D_x = 1.388\ g\,cm^{-3}$, $\mu(MoK\alpha) = 0.597\ mm^{-1}$, $S = 1.072$, $(\Delta\rho)_{max} = 0.20$, $(\Delta\rho)_{min} = -0.28\ e\,Å^{-3}$.

TABLE I Fractional atomic coordinates and equivalent isotropic displacement parameters for non-H atoms

Atom	x/a	y/b	z/c	U_{eq} (Å^2)
Mn	0.61992(4)	0.72759(3)	0.19352(4)	0.0469(2)
O(1)	0.4494(2)	0.6502(2)	0.2039(3)	0.0826(7)
O(2)	0.4517(2)	0.8314(2)	0.2703(2)	0.0694(6)
O(3)	0.7179(2)	0.5693(2)	0.1648(2)	0.0678(6)
O(4)	0.7346(2)	0.7548(1)	0.4069(2)	0.0530(5)
O(5)	0.4428(7)	1.0114(8)	0.484(1)	0.179(4)
N(1)	0.5740(2)	0.7131(2)	−0.0550(2)	0.0570(6)
N(2)	0.6743(2)	0.8847(2)	0.1409(3)	0.0548(6)
C(1)	0.3976(3)	0.7435(3)	0.2486(3)	0.0539(7)
C(2)	0.2698(2)	0.7494(2)	0.2775(3)	0.0529(7)
C(3)	0.2063(3)	0.6539(3)	0.2450(4)	0.081(1)
C(4)	0.0879(3)	0.6595(4)	0.2745(5)	0.094(1)
C(5)	0.0340(3)	0.7608(4)	0.3334(4)	0.086(1)
C(6)	0.0949(3)	0.8557(4)	0.3619(4)	0.089(1)
C(7)	0.2130(3)	0.8502(3)	0.3344(4)	0.072(1)
C(8)	0.8829(3)	0.8270(3)	0.6880(3)	0.063(1)
C(9)	0.9338(3)	0.8668(3)	0.8368(4)	0.080(1)
C(10)	0.9377(3)	0.8027(4)	0.9427(4)	0.086(1)
C(11)	0.8914(3)	0.7000(4)	0.9017(4)	0.082(1)
C(12)	0.8439(3)	0.6581(3)	0.7520(3)	0.0675(8)
C(13)	0.8396(2)	0.7216(2)	0.6428(3)	0.0505(7)
C(14)	0.7878(2)	0.6801(2)	0.4808(3)	0.0481(6)
C(15)	0.8060(3)	0.5669(2)	0.4201(3)	0.0587(7)
C(16)	0.7735(3)	0.5183(2)	0.2673(4)	0.0606(8)
C(17)	0.8088(4)	0.3948(3)	0.2207(4)	0.086(1)
C(18)	0.5303(3)	0.6209(3)	−0.1478(3)	0.0744(9)
C(19)	0.4982(4)	0.6125(4)	−0.3006(4)	0.093(1)
C(20)	0.5095(4)	0.7017(5)	−0.3597(4)	0.100(1)
C(21)	0.5549(3)	0.7988(4)	−0.2669(4)	0.084(1)
C(22)	0.5876(2)	0.8014(3)	−0.1124(3)	0.059(1)
C(23)	0.6419(2)	0.8987(2)	−0.0027(3)	0.0569(7)
C(24)	0.6600(3)	0.9973(3)	−0.0421(4)	0.077(1)
C(25)	0.7138(4)	1.0814(3)	0.0651(5)	0.093(1)
C(26)	0.7486(3)	1.0674(3)	0.2121(5)	0.086(1)
C(27)	0.7263(3)	0.9680(2)	0.2457(4)	0.0678(8)

RESULTS AND DISCUSSION

Crystal Structure

The molecular structure of the complex is illustrated in Fig. 1 with the atom numbering scheme. Selected bond distances and angles, together with atomic separations involved in H-bonds, are listed in Table II. Benzoic acid, bzac and 2,2′-bipyridine (bipy) all chelate to Mn(II) to form a six coordinate complex. Bond angles around the Mn(II) atom greatly deviate from expected values so the coordination geometry may be better described as a distorted pyramid rather than a distorted octahedron. Two N atoms from bipy and two O atoms from bzac form the basal plane, while the chelating carboxyl group of benzoic acid occupies the apical position of the pyramid with a chelating angle of 56.90(8)°. Average Mn–O (2.268(2) Å) in the apical direction is 0.166 Å longer than the Mn–O distance of 2.102(2) Å in the basal plane. The Mn(II) atoms deviates from the basal plane by 0.72 Å toward the apex of the pyramidal.

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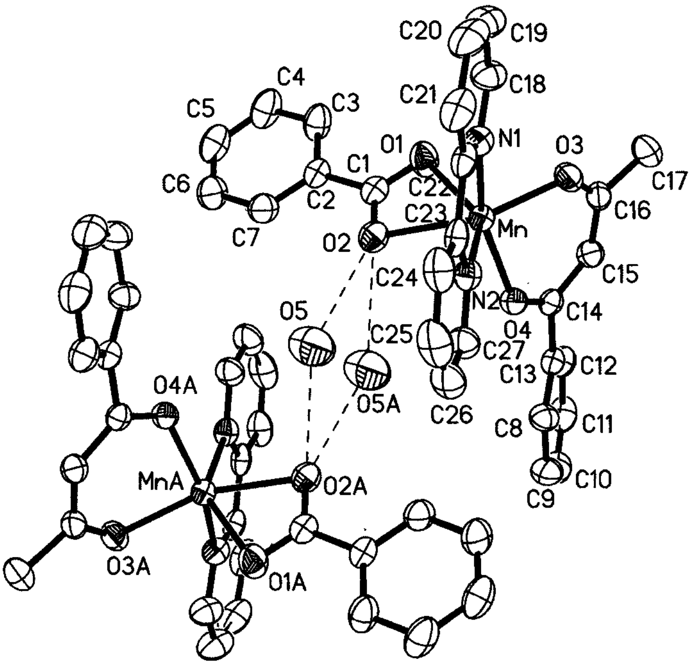

FIGURE 1 The dimeric molecular structure of the title complex with 30% probability thermal displacement ellipsoids, the dashed lines showing H-bonding. H atoms are omitted for clarity. Symmetry code (A): $1-x$, $2-y$, $1-z$.

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

Mn–O(1)	2.237(2)	Mn–O(2)	2.298(2)
Mn–O(3)	2.105(2)	Mn–O(4)	2.098(2)
Mn–N(1)	2.227(2)	Mn–N(2)	2.250(2)
O(1)–C(1)	1.241(3)	O(2)–C(1)	1.248(3)
O(3)–C(16)	1.260(4)	O(4)–C(14)	1.274(3)
C(1)–C(2)	1.495(4)	C(13)–C(14)	1.492(4)
C(14)–C(15)	1.388(4)	C(15)–C(16)	1.404(4)
C(16)–C(17)	1.510(4)	C(22)–C(23)	1.484(4)
O(5)···O(2)	2.643(9)	O(5)···O(2)A	2.790(9)
O(1)–Mn–O(2)	56.90(8)	O(1)–Mn–O(3)	91.63(9)
O(1)–Mn–O(4)	109.81(9)	O(1)–Mn–N(1)	94.24(10)
O(1)–Mn–N(2)	139.16(9)	O(2)–Mn–O(3)	146.51(9)
O(2)–Mn–O(4)	95.08(8)	O(2)–Mn–N(1)	102.98(9)
O(2)–Mn–N(2)	87.92(8)	O(3)–Mn–O(4)	84.53(8)
O(3)–Mn–N(1)	89.38(9)	O(3)–Mn–N(2)	125.58(9)
O(4)–Mn–N(1)	155.30(8)	O(4)–Mn–N(2)	91.77(9)
N(1)–Mn–N(2)	72.46(9)	C(1)–O(1)–Mn	92.8(2)
C(1)–O(1)–Mn	92.8(2)	C(1)–O(2)–Mn	89.8(2)
C(16)–O(3)–Mn	126.6(2)	C(14)–O(4)–Mn	126.7(2)
O(1)–C(1)–O(2)	120.5(3)	O(1)–C(1)–C(2)	119.6(3)
O(2)–C(1)–C(2)	119.8(3)	O(4)–C(14)–C(15)	125.0(3)
O(4)–C(14)–C(13)	115.8(2)	C(13)–C(14)–C(15)	119.1(2)
C(14)–C(15)–C(16)	125.2(3)	O(3)–C(16)–C(15)	125.4(3)
O(3)–C(16)–C(17)	116.9(3)	C(15)–C(16)–C(17)	117.6(3)

Symmetry code: (A) $1-x$, $2-y$, $1-z$.

In the present complex, the C(14)–C(15)–C(16) bond angle of 125.2(3)° implies the enol configuration of bzac, and almost identical bond distances [O(3)–C(16) 1.260(4) and O(4)–C(14) 1.274(3) Å] suggest electron delocalization within the enol ring. Keto–Enol tautomerism of 1,3-diketones such as bzac has been extensively studied [14]. Neutron diffraction and accurate low temperature X-ray diffraction reveals that within the conjugated enol ring of bzac the C–C bond furthest from the phenyl ring is slightly longer than the C–C bond nearest the phenyl ring [15,16]. The relatively longer C(15)–C(16) bond [1.404(4) Å] and shorter C(14)–C(15) bond [1.388(4) Å] in the structure agree well with the above conclusion.

The atoms of the enol ring are coplanar as expected, the maximum atomic deviation from the mean plane being 0.014(2) Å. However, the Mn(II) atom deviates from the enol ring plane by 0.550(3) Å. The dihedral angle between the enol ring plane and the plane formed by Mn, O(3) and O(4) atoms is 20.6(1)°, a value which implies a rather poor overlap of Mn and O atomic orbitals. This phenomenon is also found in other Mn(II) and Mn(III) complexes [17–19, 21]. A comparison of dihedral angles, out-of-plane values of Mn atom and Mn–O distances is summarized in Table III. It seems that out-of-plane values of Mn atoms and dihedral angles are independent of Mn–O distances. This strongly suggests the existence of electrostatic interactions between Mn atom and the bzac ligand.

The crystal structure consists of the complex and crystalline water. Because of the space between neighboring complex molecules, crystalline water molecules randomly distribute in two sites around a crystallographic inversion centre as mentioned above. Crystalline water molecules link neighboring complex molecules with H-bonding to form a supramolecular dimmer as shown in Fig. 1. Because of disordering of crystalline water the appropriate H atoms were not located in the structure. However, the O(5)···O(2) distance of 2.643(9) Å and O(5)...O(2)A distance of 2.790(9) Å clearly show intermolecular H-bonding between complex and crystalline water.

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TABLE III A comparison of structural data between the present compound and other reported species

Complex	*Deviation*[†] (Å)	*Dihedral angle*[‡] (°)	*Mn–O distances* (Å)		*Ref.*
$MnC_{45}H_{33}O_6$	0.550	21.7	2.142	1.931	[17]
	0.252	9.8	2.109	1.917	
	0.229	9.7	1.935	1.908	
$Mn_{10}C_{108}H_{76}N_6O_{36}$	0.590	25.2	1.954	1.899	[18]
$Mn_2C_{56}H_{54}F_{12}N_4O_{12}$	0.446	16.0	2.155	2.115	[19]
	0.124	4.6	2.133	2.115	
$Mn_4C_{53}H_{45}O_{17}$	0.035	1.7	1.920	1.914	[20]
	0.029	1.5	1.926	1.911	
	0.038	1.5	1.931	1.913	
$Mn_4C_{51}H_{42}N_3O_{15}$	0.266	11.3	1.919	1.881	[21]
	0.023	1.6	1.917	1.896	
	0.001	0.5	1.906	1.903	
$MnC_{27}H_{22}N_2O_4$	0.550	20.6	2.105	2.098	This work

[†] Deviation of the Mn atom from the mean plane of the enol ring; [‡] Dihedral angle between the mean plane of the enol ring and the O–Mn–O plane.

IR Spectrum

The carboxyl stretch was observed at 1453 cm^{-1} [ν_s(COO)] and 1509 cm^{-1} [ν_{as}(COO)], values which agree with the coordination fashion of the carboxyl group in the complex. The $\Delta\nu$ value (56 cm^{-1}) also agrees with those reported previously [22].

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Supplementary Material

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

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