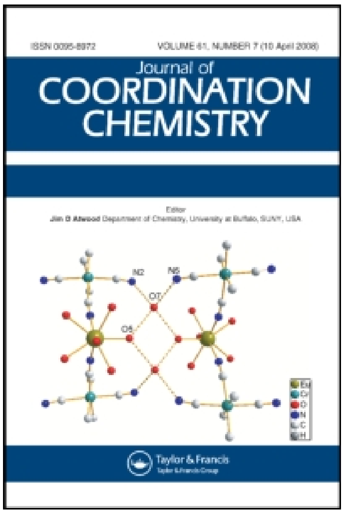

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Synthesis and crystal structure of aquachlorobis(1,10-phenanthroline)manganese(II) nitrobenzoate trihydrate

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Synthesis and crystal structure of aquachlorobis(1,10-phenanthroline)manganese(II) nitrobenzoate trihydrate

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(Recived in final form 9 September 2004)

The title compound has been prepared and its crystal structure determined by X-ray diffraction methods. The complex salt consists of Mn(II) complex cations, benzoate anions and lattice water molecules. Mn(II) assumes a distorted octahedral geometry defined by two 1,10-phenanthroline (phen) ligands, a Cl^- ion and a water molecule. A comparison of bond distances and bond angles suggests electrostatic interaction between Mn(II) and coordinated N atoms. The nitrobenzoate anion does not coordinate to the Mn atom but links with the complex cation via $O-H\cdots O$ hydrogen bonds. Aromatic stacking occurs between phen rings and between phen and benzoate.

Keywords: Manganese(II); Phenanthroline; Nitrobenzoate; Crystal structure; Aromatic stacking

1. Introduction

Aromatic stacking interactions are correlated with electron transfer in biological systems and play an important role in certain biological process [1]. Many X-ray structural investigations have shown that aromatic stacking commonly occurs in metal complexes containing aromatic heterocyclic ligands. In order to reveal the general regularity of aromatic stacking, a series of metal complexes with bithiazole [2], quinoline [3], imidazole and benzimidazole [4–6] has been prepared. As a part of this investigation of aromatic stacking in metal complexes, the title complex of Mn(II) has been prepared and its X-ray structure is presented below.

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2. Experimental

2.1. *Synthesis*

$MnCl_2 \cdot 2H_2O$ (0.17 g, 1 mmol) was dissolved in an aqueous solution (10 cm^3) of nitrobenzoic acid (0.33 g, 2 mmol) and NaOH (0.08 g, 2 mmol). The solution was refluxed for 10 min and an ethanol solution (10 cm^3) of 1,10-phenanthroline (phen) (0.36 g, 2 mmol) added with continuous stirring. The mixture was then refluxed for 2 h. After cooling to room temperature, the solution was filtered and pale yellow, single crystals were obtained from the filtrate after 2 weeks. Elemental analyses were performed on a Carlo-Erba 1160 instrument. Anal. Calc. for $C_{31}H_{28}ClMnN_5O_8$(%): C, 53.99; N, 10.16; H, 4.06. Found: C, 53.56; N, 9.96; H, 4.28. IR spectra of the complex were measured (KBr pellets) in the 4000–400 cm^{-1} range using a Nicolet 5DX FT-IR spectrophotometer.

2.2. *Crystal structure determination*

X-ray diffraction intensities of a single crystal (approximate dimensions $0.35 \times 0.32 \times 0.24$ mm) of the complex were collected on a Rigaku RAXIS-RAPID diffractometer at room temperature with Mo Kα radiation up to $2\theta = 50°$. A total of 12 125 reflections were collected, of which 5456 were independent ($R_{int} = 0.017$) and 4697 were observed with $I > 2\sigma(I)$. The usual Lp and empirical absorption corrections [7] were applied.

The crystal structure was solved by direct methods followed by Fourier syntheses. Structure refinement was performed by full-matrix least-squares procedures on F^2 using SHELX-97 [8]. H atoms on the water molecule were located in a difference Fourier map and refined in riding mode with fixed isotropic displacement parameters of 0.08 Å^2. Other H atoms were placed in calculated positions with C–H = 0.93 Å and N–H = 0.86 Å, and were included in the final cycles of refinement in riding mode, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atoms. Final $R = 0.0329$ and $wR2 = 0.0838$ for observed reflections, R = 0.0415 and $wR2 = 0.0877$ for all independent reflections, $w = 1/[\sigma^2(F_o{}^2) + (0.0467P)^2 + 0.4696P$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

2.2.1. Crystal data. $C_{31}H_{28}N_5O_8Cl$ Mn, $M = 688.97$, triclinic, space group $P\bar{1}$, $a = 10.8999(11)$, $b = 11.8618(12)$, $c = 12.8936(12)$ Å, $\alpha = 103.493(2)$, $\beta = 92.672(2)$, $\gamma = 104.668(2)°$, $V = 1558.3(3)$ Å^3, $Z = 2$, $F(000) = 710$, $D_c = 1.468$ g cm^{-3}, μ(Mo Kα) = 0.569 mm^{-1}, $S = 1.029$, $(\Delta\rho)_{max} = 0.35$, $(\Delta\rho)_{min} = -0.21$ e Å^{-3}. Full lists of crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 248007.

3. Results and discussion

3.1. *Crystal structure*

Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in table 1 and selected bond distances and angles in table 2. The molecular structure of the complex salt is illustrated in figure 1.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters for the complex salt.

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq) (Å^2)
Mn	0.32718(3)	0.11871(2)	0.80443(2)	0.0389(1)
Cl	0.44448(5)	0.14058(5)	0.97754(4)	0.0566(2)
O1	0.3886(2)	0.5310(2)	0.7545(1)	0.0763(7)
O2	0.4121(2)	0.3817(2)	0.6251(1)	0.0665(6)
O3	0.0535(3)	0.5466(2)	0.2657(2)	0.117(1)
O4	0.0181(2)	0.6845(2)	0.3918(2)	0.103(1)
O5	0.4517(1)	0.2778(1)	0.7821(1)	0.0543(5)
N1	0.4069(1)	−0.0268(1)	0.7101(1)	0.0403(5)
N2	0.2486(2)	0.0825(1)	0.6262(1)	0.0440(5)
N3	0.1731(2)	0.2089(1)	0.8579(1)	0.0432(5)
N4	0.1514(2)	−0.0303(1)	0.8205(1)	0.0432(5)
N5	0.0675(2)	0.6042(2)	0.3592(2)	0.0787(9)
C1	0.4830(2)	−0.0810(2)	0.7510(2)	0.0489(7)
C2	0.5291(2)	−0.1708(2)	0.6884(2)	0.0573(8)
C3	0.4972(2)	−0.2038(2)	0.5804(2)	0.0562(8)
C4	0.4170(2)	−0.1494(2)	0.5336(2)	0.0468(6)
C5	0.3784(2)	−0.1801(2)	0.4211(2)	0.0594(8)
C6	0.2999(2)	−0.1272(2)	0.3799(2)	0.0613(8)
C7	0.2523(2)	−0.0366(2)	0.4468(2)	0.0496(6)
C8	0.1723(2)	0.0228(2)	0.4075(2)	0.0643(8)
C9	0.1336(2)	0.1095(2)	0.4758(2)	0.0666(9)
C10	0.1744(2)	0.1369(2)	0.5852(2)	0.0555(7)
C11	0.2891(2)	−0.0038(2)	0.5579(1)	0.0402(6)
C12	0.3728(2)	−0.0607(2)	0.6024(1)	0.0387(6)
C13	0.1844(2)	0.3264(2)	0.8777(2)	0.0528(7)
C14	0.0857(2)	0.3770(2)	0.9082(2)	0.0627(8)
C15	−0.0287(2)	0.3038(2)	0.9179(2)	0.0641(9)
C16	−0.0458(2)	0.1789(2)	0.8986(2)	0.0510(7)
C17	−0.1618(2)	0.0956(3)	0.9101(2)	0.0634(9)
C18	−0.1724(2)	−0.0230(3)	0.8922(2)	0.0617(8)
C19	−0.0682(2)	−0.0706(2)	0.8606(2)	0.0498(7)
C20	−0.0734(2)	−0.1935(2)	0.8420(2)	0.0612(8)
C21	0.0315(2)	−0.2311(2)	0.8152(2)	0.0637(8)
C22	0.1419(2)	−0.1469(2)	0.8059(2)	0.0539(7)
C23	0.0478(2)	0.0080(2)	0.8487(1)	0.0409(6)
C24	0.0592(2)	0.1353(2)	0.8684(1)	0.0421(6)
C25	0.2920(2)	0.5064(2)	0.5796(2)	0.0474(6)
C26	0.2928(2)	0.4633(2)	0.4704(2)	0.0618(8)
C27	0.2210(3)	0.4958(2)	0.3973(2)	0.0684(9)
C28	0.1474(2)	0.5715(2)	0.4357(2)	0.0583(8)
C29	0.1453(2)	0.6172(2)	0.5432(2)	0.0630(8)
C30	0.2183(2)	0.5842(2)	0.6152(2)	0.0576(8)
C31	0.3714(2)	0.4705(2)	0.6593(2)	0.0509(7)
O1W	0.6815(2)	0.4076(2)	0.8911(2)	0.0905(8)
O2W	0.6311(2)	0.6255(2)	0.8682(2)	0.0892(8)
O3W	0.2910(2)	0.6659(2)	0.9141(2)	0.0810(7)

The salt consists of complex Mn(II) cations, nitrobenzoate anions and lattice water molecules. A Cl$^-$ anion and a water molecule coordinate *cis* to Mn(II) and two phen ligands act as chelates to complete a distorted octahedral coordination geometry. Phen ligands chelating to the same Mn(II) atom are nearly perpendicular to each other with a dihedral angle of 87.11(4)°. The Cl–Mn–N2 [168.46(5)°] and O5–Mn–N4 [165.07(6)°] angles are normal, but the N1–Mn–N3 angle of 155.82(6)° is significantly smaller than the expected value. This implies poor overlap of atomic orbitals between Mn and N1 and N3. The Mn–N1 [2.256(2) Å] and

Table 2. Selected bond distances (Å) and angles (°) for the complex.

Mn–Cl	2.4453(6)	Mn–O5	2.116(2)
Mn–N1	2.256(2)	Mn–N2	2.317(2)
Mn–N3	2.261(2)	Mn–N4	2.309(2)
O1–C31	1.248(3)	O2–C31	1.240(3)
O3–N5	1.220(4)	O4–N5	1.212(3)
N5–C28	1.467(3)	C25–C31	1.515(3)
Cl–Mn–O5	92.30(4)	Cl–Mn–N1	96.19(4)
Cl–Mn–N2	168.46(5)	Cl–Mn–N3	100.76(4)
Cl–Mn–N4	96.62(4)	O5–Mn–N1	102.61(6)
O5–Mn–N2	85.77(6)	O5–Mn–N3	93.86(6)
O5–Mn–N4	165.07(6)	N1–Mn–N2	73.21(6)
N1–Mn–N3	155.82(6)	N1–Mn–N4	88.33(6)
N2–Mn–N3	90.72(6)	N2–Mn–N4	87.77(6)
N3–Mn–N4	72.76(6)		

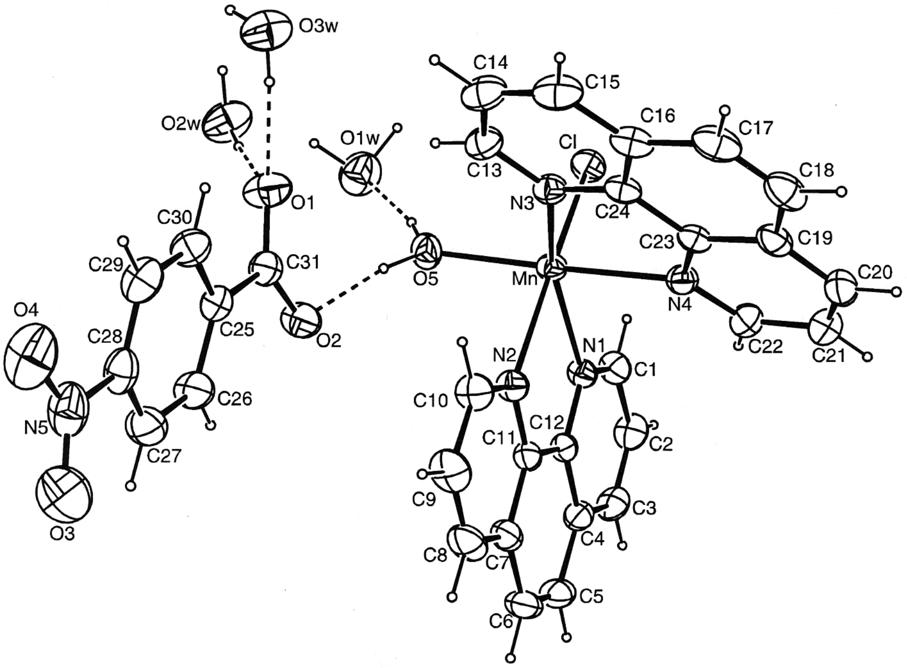

Figure 1. The molecular structure of the salt drawn with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding.

Mn–N3 [2.261(2) Å] bonds are appreciably shorter than the Mn–N2 [2.317(2) Å] and Mn–N4 [2.309(2) Å] bonds. This suggests a more electrostatic interaction between Mn and coordinated N atoms, in agreement with the situation found in other related Mn complexes [9].

Parallel phen rings of neighboring cations overlap each other as shown in figure 2. The interplanar distances between N1-phen (phen containing N1) and $N1^{i}$-phen (symmetry code: $1-x$, $-y$, $1-z$) and between N3-phen and $N3^{ii}$-phen

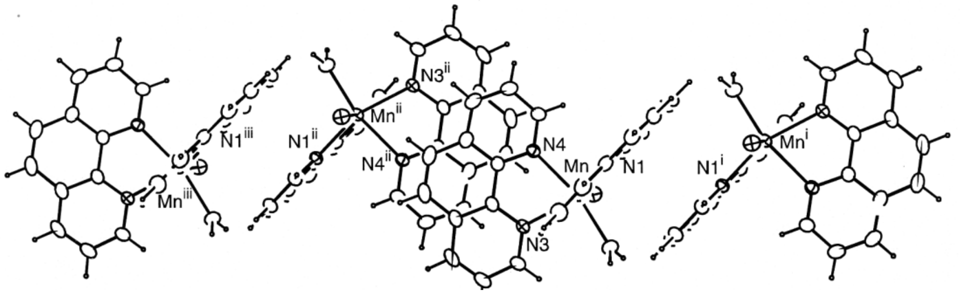

Figure 2. Aromatic π–π stacking between phenanthroline rings of neighboring complex molecules (symmetry codes used are (i): $1-x$, $-y$, $1-z$; (ii): $-x$, $-y$, $2-z$; (iii): $-1+x$, y, $1+z$).

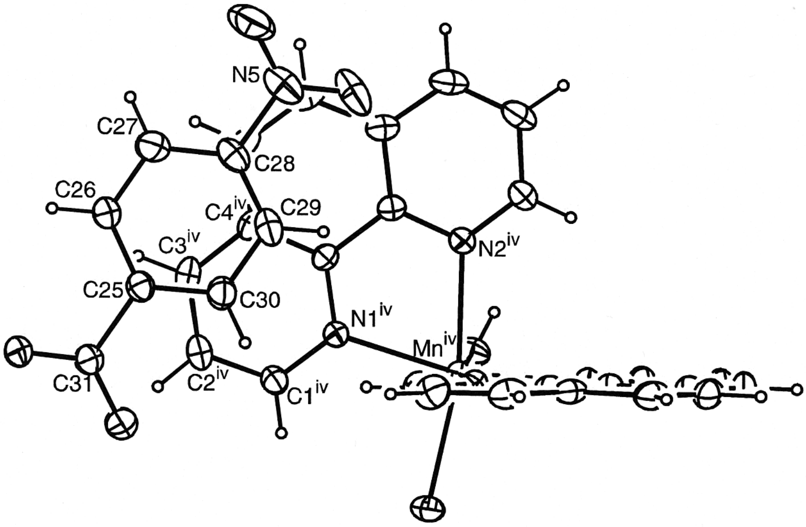

Figure 3. Aromatic π–π stacking between phenanthroline and the benzene ring of nitrobenzoate (symmetry code is (iv): x,$-1+y$, z).

(symmetry code: $-x$, $-y$, $2-z$) are 3.492(5) and 3.445(4) Å, respectively. This clearly indicates the existence of aromatic π–π stacking between the phen rings. In addition, N1^{iv}-phen (symmetry code: x, $-1+y$, z) and the benzene ring of nitrobenzoate are nearly parallel [dihedral angle 8.2(1)°] and partially overlap as shown in figure 3. Distances between C3^{iv} and C4^{iv} and the benzene ring are 3.488(3) and 3.526(2) Å, respectively, also suggesting the existence of aromatic π–π stacking between phen and benzene rings.

An extensive hydrogen-bonding network occurs in the crystal (table 3). Benzoate anions link with complex cations through the carboxyl group (O2) and coordinated water (O5), and both lattice water molecules O2w and O3w simultaneously bridge complex cations and nitrobenzoate anions to form a centrosymmetric supramolecular dimer.

Table 3. Hydrogen bonding parameters (Å, °) for the complex salt.

Donor	H	Acceptor	D–H	H···A	D···A	D–H–A
O1W	H1A	O2W	0.95	1.96	2.851(3)	157
O1W	H1B	O3W^{v}	0.95	1.96	2.871(3)	161
O2W	H2A	O1	0.84	1.95	2.787(3)	172
O2W	H2B	Cl^{v}	0.91	2.46	3.326(2)	160
O3W	H3A	O1	0.86	1.87	2.730(3)	173
O3W	H3B	Cl^{v}	0.90	2.31	3.211(2)	174
O5	H5A	O1W	0.85	1.87	2.707(3)	170
O5	H5B	O2	0.87	1.81	2.675(2)	171

Symmetry code used is (v): $1 - x$, $1 - y$, $2 - z$.

3.2. *IR spectra*

IR spectra of the title complex were assigned based on the crystal structure. Stretching of the carboxyl group was observed at 1578 cm^{-1} [ν_{as}(coo)] and 1427 cm^{-1} [ν_{s}(coo)]. The $\Delta\nu$ value of 151 cm^{-1} agrees with the uncoordinated mode of the carboxyl group [10]. The water stretch appears at 3457 cm^{-1}. Compared to the range of 3580–3650 cm^{-1} found for the "free" hydroxyl group, the lower frequency $\nu(H_2O)$ value is an indication of the participation of lattice water molecules in hydrogen bonding.

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