Synthesis and Crystal Structure of Tetraethylammonium Tris(1,10-phenanthroline)manganese(II) triperchlorate (Et₄N)[Mn(phen)₃](ClO₄)₃

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The title complex was serendipitously obtained by reacting imidazole-4,5-dicarboxylic acid, tetraethylammonium hydroxide, 1,10-phenanthroline, and manganese(II) perchlorate hexahydrate in ethanol-water mixed solvent. It crystallizes in the monoclinic system, space group *Cc* with *a* = 24.8043(6), *b* = 8.7973(2), *c* = 24.2475(2) Å, *β* = 118.844(1)°, *V* = 4634.6(2) Å³ and *Z* = 4. A most noteworthy structural feature is that two counterions, namely Et₄N⁺ and ClO₄[−] cocrystallize in the crystal lattice.

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Tris(1,10-phenanthroline) metal complexes have received considerable attention in the field of biomedicine, because, for example, they can effectively interact with DNA in various binding modes, and they often exhibit racemization in solid-state phase.^{1,2} The central metal variation in these complexes may facilitate a certain application, or provide easy access to study of the mechanism of specific functions. Manganese complexes of this type are particularly attractive, owing to their special utility as antifungal, and contraceptive and antivenereal agents.³ Some structural variations in [Mn(phen)₃]²⁺ moieties of previously reported complexes are usually found.⁴ For a better understanding of mechanisms associated with a specific function, knowledge of more crystal structures is fundamentally required. Here, we report on the structure of the title complex, (Et₄N)[Mn(phen)₃](ClO₄)₃.

The complex is serendipitously isolated from a reaction system containing imidazole-4,5-dicarboxylate, 1,10-phenanthroline and manganese(II) perchlorate in the presence of tetraethylammonium salts. Imidazole-4,5-dicarboxylic acid (1 mmol), dissolved in water (25 ml), was neutralized with tetraethylammonium hydroxide (2 mmol), and was added dropwise to an ethanol (25 ml) solution containing manganese(II) perchlorate hexahydrate (2 mmol) and 1,10-phenanthroline (2 mmol) with continuous stirring. The resulting suspension was refluxed for 1 d and then filtered. The

filtrate was allowed to stand undisturbed for one week or so at room temperature, during which time red needle-shape crystals of the title complex are deposited.

Diffraction data were collected on a Siemens SMART CCD area-detector diffractometer by using graphite monochromated Mo *K*_α radiation (*λ* = 0.71073 Å) at 293(2)K. Lorentz-polarization correction and integration of data were performed with the SAINT package, while empirical absorption correction was applied by using SADABS. The structure was solved by a combination of direct methods and difference Fourier syntheses, and refined on *F*² by full-matrix least-squares methods using the SHELXTL-97 program package, with anisotropic thermal parameters for the non-hydrogen atoms. H atoms were introduced at the calculated positions and refined as riding atoms. Intensity statistics and systematic absence exceptions in the reflection data favor a noncentric space group, *Cc*. However, its absolute structure parameter was found to be 0.40(5), indicative of racemic twinning. The structure was

Fig. 1 Chemical structure of the title complex.

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Table 1 Crystal and experimental data of the title complex

Empirical formula	C ₄₄ H ₄₄ Cl ₃ MnN ₇ O ₁₂
Formula weight	1024.15
Crystal system	monoclinic
Space group, <i>Z</i>	<i>Cc</i> , 4
<i>a</i>	24.8043(6) Å
<i>b</i>	8.7973(2) Å
<i>c</i>	24.2475(2) Å
<i>β</i>	118.844(1)°
<i>V</i>	4634.6(2) Å ³
<i>D_x</i>	1.468 Mg/m ^{−3}
Absorption coefficient	0.528 mm ^{−1}
<i>θ</i> range for data collection	1.87 to 25.06°
Reflections collected/unique	7205/4590 [<i>R</i> _{int} = 0.0369]
Goodness-of-fit on <i>F</i> ²	1.001
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> = 0.0799, <i>wR</i> = 0.1874
(Δσ) _{max}	0.001
(Δρ) _{max,min}	0.757 and −0.297 e. Å ^{−3}
Measurement	Siemens SMART CCD
Program system	SHELXTL-97
Structural determination	Direct method
Refinement	full matrix

Table 2 Selected bond distances (Å) and angles (°)

Bond distances			
Mn1–N1	2.229(9)	Mn1–N2	2.258(9)
Mn1–N3	2.232(9)	Mn1–N4	2.262(10)
Mn1–N6	2.233(10)	Mn1–N5	2.268(11)
Bond angles			
N1–Mn1–N3	90.4(3)	N6–Mn1–N4	95.5(4)
N1–Mn1–N6	166.3(3)	N2–Mn1–N4	170.3(3)
N3–Mn1–N6	98.4(3)	N1–Mn1–N5	98.0(3)
N1–Mn1–N2	73.8(3)	N3–Mn1–N5	169.1(4)
N3–Mn1–N2	101.5(3)	N6–Mn1–N5	74.8(4)
N6–Mn1–N2	94.0(3)	N2–Mn1–N5	87.6(3)
N1–Mn1–N4	96.9(4)	N4–Mn1–N5	96.7(4)
N3–Mn1–N4	75.2(4)

Fig. 2 The structural drawing of the $[\text{Mn}(\text{phen})_3]^{2+}$ cation in the title complex, showing 30% probability displacement ellipsoids.

therefore refined using a TWIN refinement routine of SHELXTL. Efforts to solve this structure in centrosymmetric $C2/c$ were unsuccessful. Some disorder both amongst the perchlorate anions and in the tetraethylammonium cation was observed, although this was not modelled. Further details of crystal data collection and refinement for the title complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

The title complex (Fig. 1) consists of a monomeric $[\text{Mn}(\text{phen})_3]^{2+}$ cation, an Et_4N^+ cation and three perchlorate anions. As shown in Fig. 2, the Mn^{II} atom is surrounded by three bidentate phen ligands, coordinated *via* six N atoms, and displays a strong distorted octahedral geometry, with *cis* angles subtended at the Mn atom, ranging from 73.8(3) to 101.5(3)° (Table 2). The central Mn atom is close to coplanarity with the four N atoms (N1, N2, N4 and N6), with the largest deviation being 0.095(4) Å for atom N1 from the plane. The Mn–N bond lengths in a narrow range from 2.229(9) to 2.268(11) Å and the tight N–Mn–N chelate angles [73.8(3), 74.8(4) and 75.2(4)°] are as expected for Mn^{II} complexes containing $[\text{Mn}(\text{phen})_3]^{2+}$.⁴ The three phen ligands are each reasonably planar, and the dihedral angles between each pair, ranging from 87.5(1) to 92.0(1)°, are indicative of approximate perpendicularity to each other.

Table 3 C–H...O hydrogen-bonding and Cl–O...Cg^a interactions (Å, °)

D–H...O	D–H	H...O	D...O	D–H...O
C1–H1A...O1	0.93	2.56	3.33(2)	139.6
C8–H8A...O9_\$1	0.93	2.35	3.17(3)	145.9
C10–H10A...O2_\$1	0.93	2.53	3.27(2)	137.4
C13–H13A...O6_\$2	0.93	2.56	3.44(2)	159.5
C14–H14A...O5_\$2	0.93	2.59	3.24(2)	127.1
C15–H15A...O3_\$3	0.93	2.57	3.32(3)	137.8
C21–H21A...O9_\$4	0.93	2.35	3.09(3)	136.8
C26–H26A...O6_\$5	0.93	2.59	3.25(2)	128.6
C27–H27A...O2_\$6	0.93	2.52	3.38(2)	153.4
C30–H30A...O8_\$1	0.93	2.43	3.22(2)	143.0
C44–H44B...O10_\$3	0.96	2.46	3.34(4)	152.1
HCl–O...Cg	Cl–O	O...Cg	Cl...Cg	Cl–O...Cg
Cl3–O10...Cg1_\$7	1.358(14)	3.5860	4.3228	114
Cl1–O1...Cg1	1.416(17)	3.3668	4.6161	147
Cl2–O8...Cg2_\$8	1.39(2)	3.7561	4.4985	114
Cl2–O7...Cg2_\$9	1.33(2)	3.3306	4.3079	130
Cl1–O2...Cg3_\$10	1.331(14)	3.8424	4.5583	115
Cl1–O1...Cg4	1.416(17)	3.4029	4.2371	117
Cl2–O6...Cg5_\$8	1.380(13)	3.1105	4.2675	141
Cl2–O5...Cg6_\$9	1.393(14)	3.1151	4.1043	127

a. Cg is the centroid of π -ring; Cg1, Cg2, Cg3, Cg4, Cg5 and Cg6 denote the centroids of the C16–C19/C23/C24 ring, the C4–C7/C11/C12 ring, the N6/C31–C35 ring, the N4/C19–C23 ring, the N2/C7–C11 ring and the N1/C1–C4/C12 ring, respectively.

Symmetry operations. \$1: x, 1-y, -1/2+z; \$2: $-1/2+x, 1/2-y, z-1/2$; \$3: $x, -1+y, z$; \$4: $1/2+x, 1/2+y, z$; \$5: $-1/2+x, 3/2-y, -1/2+z$; \$6: $x, 2-y, -1/2+z$; \$7: $-1/2+x, 1/2+y, z$; \$8: $1/2+x, 1/2-y, 1/2+z$; \$9: $1/2+x, 3/2-y, 1/2+z$; \$10: $x, 1-y, 1/2+z$.

The title complex mainly differs from other reported $[\text{Mn}(\text{phen})_3]^{2+}$ -containing species by the coexistence of two electric charge counterparts, namely the Et_4N^+ cation and the ClO_4^- anion in the crystal lattice. The co-crystallized salt extrudes any solvent molecules that might form hydrogen bonds within the crystal lattice.

The extensive intra- and inter-molecular C–H...O hydrogen-bonding interactions (Table 3) involving phen ligands, tetraethylammonium and perchlorate ions with C...O separations in the range 3.090(5)–3.444(3) Å, as well as complicated Cl–O...Cg (Cg is the centroid of π -ring) interactions with O...Cg separations shorter than 4.0 Å, are observed in the crystal structure. These hydrogen bonding interactions together with numerous van der Waals contacts ensure the crystalline cohesion of the title complex.

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