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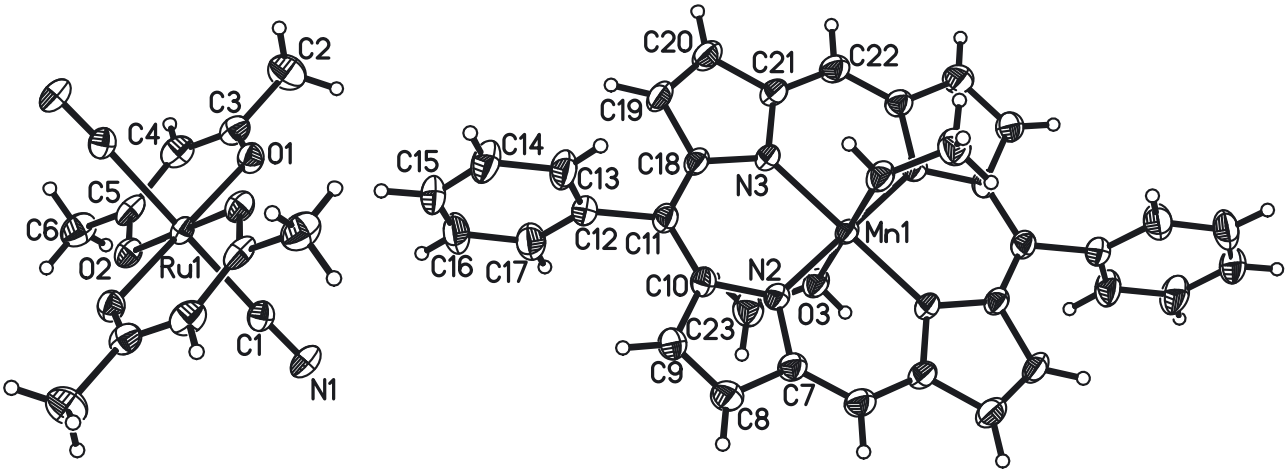
The crystal structure of dimethanol-5,15-diphenylporphyrin-21,23-diido-κ^4*N,N′,N″,N‴*-manganese(III) *trans*-dicyanido-bis(acetylacetonato-κ^2O,O′)ruthenium(III), $C_{46}H_{42}N_6O_6RuMn$



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Abstract

$C_{46}H_{42}N_6O_6RuMn$, triclinic, $P\bar{1}$ (no. 2), a = 8.2340(8) Å, b = 9.7872(10) Å, c = 13.5397(14) Å, α = 83.646(2)°, β = 77.599(2)°, γ = 80.615(2)°, V = 1048.17(18) Å^3, Z = 1, $R_{gt}(F)$ = 0.0342, w$R_{ref}(F^2)$ = 0.0910, T = 293 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Block, dark-red
Size:	0.13 × 0.11 × 0.09 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.72 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5210, 3643, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 3080
$N(param)_{refined}$:	277
Programs:	Bruker programs [1], SHELX [2, 3]

Source of materials

The manganese precursor $[Mn(DPP)(H_2O)_2]ClO_4$ (H_2DPP = 5,15-diphenylporphyrin) was prepared by refluxing the mixture of H_2DPP and $[Mn(ClO_4)_2]\cdot 6H_2O$ with molar ratio of 1:1 in DMF for 6–7 h under air atmosphere. A methanol/water (5:1, v:v) (10 mL) solution of $[Ph_4P][Ru(acac)_2(CN)_2].H_2O$ (acac = acetylacetonato) (0.10 mmol, 71.0 mg) was carefully added into another solution formed by $[Mn(DPP)(H_2O)_2]ClO_4$ (0.10 mmol, 65.1 mg) dissolved in methanol (10 mL). The resulting mixture was filtered after several minutes stirring and the filtrate was put in the dark with no disturbation for

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

	x	*y*	*z*	U_{iso}*/U_{eq}
Ru1	0.500000	0.000000	0.500000	0.03471 (13)
Mn1	1.000000	1.000000	0.000000	0.03594 (17)
O1	0.3664 (2)	0.1740 (2)	0.45071 (16)	0.0445 (5)
O2	0.3878 (2)	−0.1164 (2)	0.42926 (15)	0.0440 (5)
O3	0.9620 (3)	0.9134 (2)	−0.13892 (16)	0.0496 (5)
H3A	1.034622	0.927984	−0.191693	0.060*
N1	0.7988 (3)	0.0345 (3)	0.3073 (2)	0.0526 (7)
N2	1.0974 (3)	0.8114 (2)	0.05292 (18)	0.0403 (6)
N3	0.7718 (3)	0.9643 (2)	0.07626 (18)	0.0395 (6)
C1	0.6915 (4)	0.0194 (3)	0.3744 (2)	0.0396 (7)
C2	0.1395 (5)	0.3211 (4)	0.4011 (3)	0.0717 (11)
H2A	0.106502	0.364655	0.463879	0.107*
H2B	0.041451	0.315586	0.374913	0.107*
H2C	0.212470	0.374938	0.353007	0.107*
C3	0.2307 (4)	0.1769 (3)	0.4191 (2)	0.0468 (8)
C4	0.1682 (4)	0.0623 (4)	0.4001 (3)	0.0534 (8)
H4	0.061827	0.077862	0.384396	0.064*
C5	0.2481 (4)	−0.0742 (4)	0.4020 (2)	0.0478 (8)
C6	0.1710 (4)	−0.1848 (4)	0.3673 (3)	0.0671 (10)
H6A	0.188646	−0.176503	0.294579	0.101*
H6B	0.052684	−0.173945	0.395340	0.101*
H6C	0.222611	−0.274736	0.389801	0.101*
C7	1.2647 (4)	0.7534 (3)	0.0327 (2)	0.0473 (8)
C8	1.2837 (4)	0.6213 (4)	0.0873 (3)	0.0606 (10)
H8	1.384128	0.561661	0.086540	0.073*
C9	1.1330 (4)	0.5972 (3)	0.1397 (3)	0.0567 (9)
H9	1.109622	0.518317	0.182067	0.068*
C10	1.0136 (4)	0.7155 (3)	0.1187 (2)	0.0449 (7)
C11	0.8420 (4)	0.7309 (3)	0.1580 (2)	0.0447 (7)
C12	0.7729 (4)	0.6159 (3)	0.2289 (3)	0.0503 (8)
C13	0.7444 (5)	0.6233 (4)	0.3313 (3)	0.0665 (10)
H13	0.768268	0.700147	0.357301	0.080*
C14	0.6801 (5)	0.5173 (4)	0.3969 (3)	0.0771 (12)
H14	0.663413	0.522557	0.466617	0.092*
C15	0.6414 (5)	0.4055 (4)	0.3602 (4)	0.0782 (13)
H15	0.599705	0.333974	0.404477	0.094*
C16	0.6639 (6)	0.3990 (4)	0.2581 (4)	0.0835 (14)
H16	0.634508	0.323894	0.232786	0.100*
C17	0.7303 (5)	0.5035 (4)	0.1916 (3)	0.0723 (11)
H17	0.746238	0.497968	0.121935	0.087*
C18	0.7317 (4)	0.8471 (3)	0.1380 (2)	0.0420 (7)
C19	0.5562 (4)	0.8669 (4)	0.1796 (3)	0.0524 (8)
H19	0.497065	0.803208	0.222913	0.063*
C20	0.4916 (4)	0.9926 (4)	0.1456 (3)	0.0579 (9)
H20	0.379469	1.032271	0.161069	0.069*
C21	0.6245 (4)	1.0550 (3)	0.0816 (2)	0.0458 (7)
C22	0.6097 (4)	1.1845 (3)	0.0309 (3)	0.0534 (8)
H22	0.502752	1.235741	0.040563	0.064*
C23	0.9244 (5)	0.7774 (4)	−0.1392 (3)	0.0659 (10)
H23A	1.023025	0.711308	−0.134879	0.099*
H23B	0.888050	0.768926	−0.200714	0.099*
H23C	0.836637	0.759644	−0.082035	0.099*

about one week at room temperature. The title dark-red block crystals were obtained by filtration with the yield of 51.3 mg (55.1%).

Experimental details

The coordinates of hydrogen atoms were added using riding models; the corresponding U_{iso} values were set to $1.2U_{eq}$ or $1.5U_{eq}$ of the parent atoms.

Comment

Porphyrin derivatives, which have attracted continuous and extensive interest over a long time in a wide range of fields including life science, chemistry, physics, and material sciences because of their excellent chemical and physical properties [4–7]. These ligands can coordinate with many magnetic metal centers to assemble molecular magnetic systems. Among which, due to the large spin state ($S = 2$) and the usually negative magnetic anisotropy, the Mn(III) ion plays an important role in magnetism. Therefore the manganese(III) porphyrin derivatives are worth to be investigated systematically towards preparing molecular magnetic materials [8–12].

As shown in the Figure, the title salt is comprised by one $[Mn(DPP)(CH_3OH)_2]^+$ cation and one $[Ru(acac)_2(CN)_2]^-$ anion. The Ru ion in the cyano precursor is coordinated by four O atoms of two acetylacetonato ions and two C atoms of cyano groups in trans position, forming a hexa-coordinated octahedron. The Ru–O bond lengths are 2.009(2) and 2.003(2) Å, respectively, with the inconspicuous difference from the Ru–C 2.071(3) Å, demonstrating the only slightly distorted octahedral geometry around the Ru(III) ion. The coordination sphere for the Mn(III) ion (located on an inversion center) in the title complex is also described as a distorted octahedral, in which four positions are occupied by four pyrrole N atoms [13] located in a perfect equatorial plane and the other two come from two O atoms of the two coordinated methanol molecules. Different from the bond parameters around the Ru(III) ion, the axial Mn–$O_{methanol}$ bond length 2.246(2) Å is obviously longer than the equatorial Mn–N bond lengths (2.005(2) and 2.009(2) Å), providing clear information about the axial markedly elongated octahedral around the Mn(III) ion, typically resulted from the proverbial Jahn–Teller effect.

Dependent on the strong intermolecular O-H···N interactions with the D···A = 2.735(6) Å and <DHA = 177.6(9)° between the N atom of the cyanide group and the O atom of the methanol molecule, the cations and anions in the ion-pair complex can be further linked into a chain structure.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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