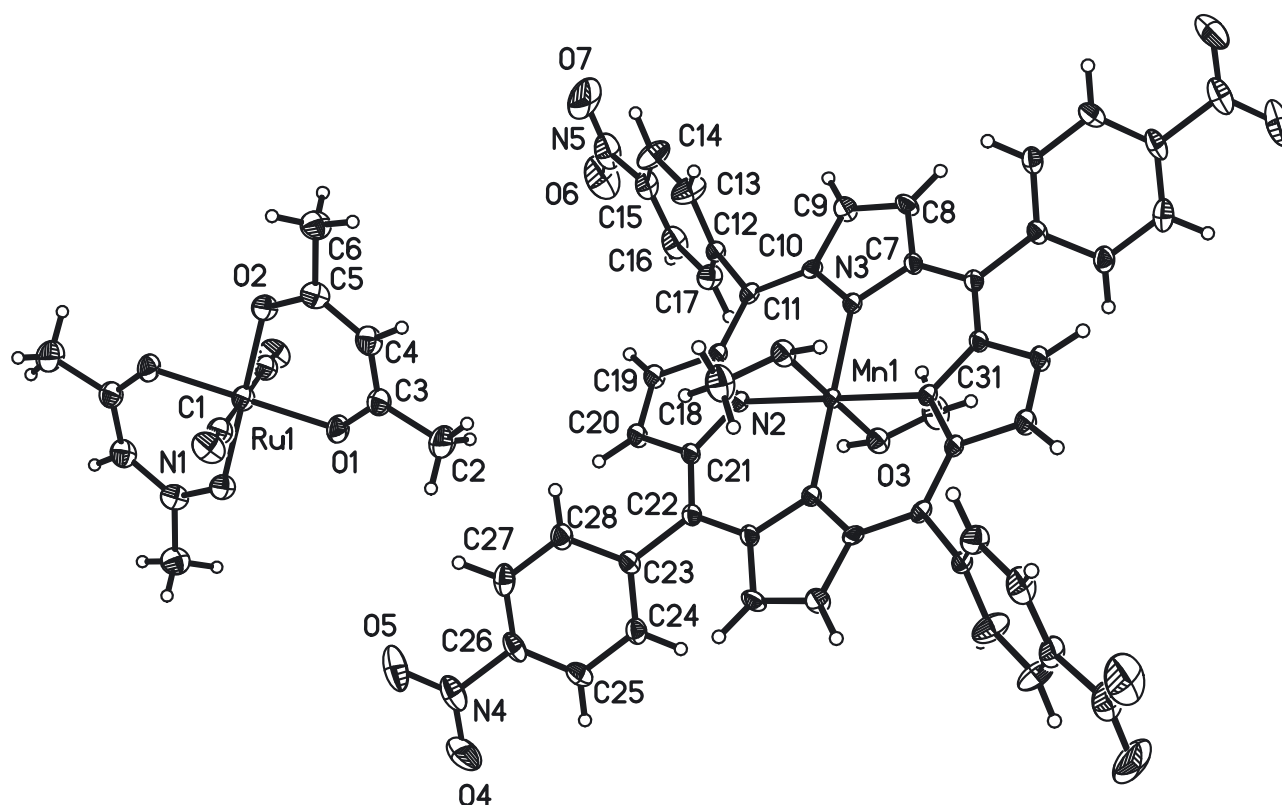


Tingting Zhou*

The crystal structure of dimethanol- $\kappa^1\text{O}$ -(5,10,15,20-tetrakis(4-nitrophenyl)porphyrin-21,23-diido- $\kappa^4\text{O},\text{O}',\text{O}'',\text{O}'''$)manganese(III) trans-dicyanido- $\kappa^1\text{C}$ -bis(acetylacetonato- $\kappa^2\text{O},\text{O}'$)ruthenium(III), $\text{C}_{58}\text{H}_{46}\text{N}_{10}\text{O}_{14}\text{RuMn}$



<https://doi.org/10.1515/ncrs-2022-0349>

Received July 10, 2022; accepted August 26, 2022;

published online September 5, 2022

$\chi = 93.430(4)^\circ$, $V = 1355.4(5) \text{ \AA}^3$, $Z = 1$, $R_{\text{gt}}(F) = 0.0509$, $wR_{\text{ref}}(F^2) = 0.1400$, $T = 293 \text{ K}$.

CCDC no.: 2203606

Abstract

$\text{C}_{58}\text{H}_{46}\text{N}_{10}\text{O}_{14}\text{RuMn}$, triclinic, $P\bar{1}$ (no. 2), $a = 8.0148(18) \text{ \AA}$, $b = 12.141(3) \text{ \AA}$, $c = 14.843(3) \text{ \AA}$, $\alpha = 107.379(4)^\circ$, $\beta = 98.415(4)^\circ$,

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

*Corresponding author: Tingting Zhou, College of Chemical Engineering and Environmental Chemistry, Weifang University, Weifang, 261061, Shandong, P. R. China, E-mail: zhoutingting1986@163.com. <https://orcid.org/0000-0002-8468-335X>

Source of material

To a solution of $[\text{Mn}(\text{TNPP})(\text{H}_2\text{O})_2]\text{ClO}_4$ [4] (TNPP = 5,10,15,20-tetrakis(4-nitrophenyl)porphyrinato) (0.10 mmol, 98.3 mg) in

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.21 × 0.15 × 0.13 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.59 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX II, φ and ω
θ_{max} , completeness:	25.0°, 98%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6469, 4688, 0.032
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3008
$N(\text{param})_{\text{refined}}$:	385
Programs:	Bruker [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Ru1	1.000000	0.000000	0.000000	0.0364 (2)
Mn1	1.000000	1.000000	0.500000	0.0230 (3)
O1	1.0780 (5)	0.1705 (3)	0.0538 (2)	0.0439 (10)
O2	0.7713 (5)	0.0265 (3)	0.0353 (2)	0.0418 (9)
O3	1.1050 (4)	1.0957 (3)	0.4038 (2)	0.0354 (9)
H3A	1.118730	1.041372	0.358203	0.042*
O4	1.8672 (8)	0.4597 (5)	0.3721 (4)	0.0933 (18)
O5	1.6553 (7)	0.3326 (5)	0.3468 (4)	0.0854 (17)
O6	0.4053 (8)	0.5751 (5)	−0.1449 (4)	0.106 (2)
O7	0.2107 (8)	0.5299 (5)	−0.0717 (4)	0.108 (2)
N1	1.1198 (6)	−0.0175 (5)	0.2123 (3)	0.0560 (14)
N2	1.0079 (5)	0.8529 (3)	0.3933 (2)	0.0241 (9)
N3	0.7685 (5)	1.0202 (3)	0.4356 (2)	0.0249 (9)
N4	1.7174 (8)	0.4318 (5)	0.3669 (3)	0.0562 (14)
N5	0.3459 (9)	0.5814 (5)	−0.0726 (4)	0.0720 (19)
C1	1.0808 (7)	−0.0138 (5)	0.1354 (4)	0.0431 (14)
C2	1.1093 (9)	0.3582 (5)	0.1637 (5)	0.075 (2)
H2A	1.225376	0.348465	0.183780	0.112*
H2B	1.062579	0.399728	0.218488	0.112*
H2C	1.103906	0.401273	0.118828	0.112*
C3	1.0094 (8)	0.2416 (5)	0.1171 (4)	0.0465 (15)
C4	0.8563 (8)	0.2171 (5)	0.1426 (4)	0.0483 (15)
H4	0.825020	0.273811	0.192988	0.058*
C5	0.7425 (7)	0.1164 (5)	0.1010 (4)	0.0434 (14)
C6	0.5720 (8)	0.1099 (5)	0.1294 (4)	0.0560 (17)
H6A	0.486247	0.109989	0.076969	0.084*
H6B	0.567258	0.175718	0.183906	0.084*
H6C	0.552835	0.039794	0.145453	0.084*
C7	0.6729 (6)	1.1122 (4)	0.4648 (3)	0.0266 (11)
C8	0.5247 (6)	1.0971 (4)	0.3929 (3)	0.0340 (12)
H8	0.440563	1.146792	0.394752	0.041*
C9	0.5298 (6)	0.9988 (4)	0.3230 (3)	0.0362 (13)
H9	0.448178	0.966897	0.268207	0.043*
C10	0.6803 (6)	0.9519 (4)	0.3466 (3)	0.0252 (11)
C11	0.7380 (6)	0.8533 (4)	0.2869 (3)	0.0259 (11)
C12	0.6277 (6)	0.7901 (4)	0.1918 (3)	0.0291 (12)
C13	0.4750 (8)	0.7312 (5)	0.1881 (4)	0.0558 (18)
H13	0.435208	0.735636	0.244718	0.067*
C14	0.3774 (8)	0.6643 (6)	0.1003 (4)	0.0626 (19)
H14	0.272356	0.625227	0.097349	0.075*

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
C15	0.4428 (8)	0.6586 (5)	0.0194 (4)	0.0476 (16)
C16	0.5914 (8)	0.7198 (5)	0.0210 (4)	0.0519 (17)
H16	0.629325	0.716790	−0.035883	0.062*
C17	0.6860 (7)	0.7869 (5)	0.1084 (3)	0.0401 (14)
H17	0.787929	0.829321	0.110565	0.048*
C18	0.8897 (6)	0.8100 (4)	0.3093 (3)	0.0264 (11)
C19	0.9452 (6)	0.7075 (4)	0.2495 (3)	0.0334 (12)
H19	0.888106	0.661400	0.189651	0.040*
C20	1.0926 (6)	0.6898 (4)	0.2945 (3)	0.0329 (12)
H20	1.156796	0.629454	0.271559	0.040*
C21	1.1351 (6)	0.7808 (4)	0.3850 (3)	0.0262 (11)
C22	1.2813 (6)	0.7924 (4)	0.4521 (3)	0.0280 (11)
C23	1.3968 (6)	0.6990 (4)	0.4321 (3)	0.0281 (11)
C24	1.5657 (7)	0.7229 (4)	0.4303 (3)	0.0349 (13)
H24	1.610083	0.799758	0.444134	0.042*
C25	1.6722 (7)	0.6366 (5)	0.4086 (4)	0.0405 (14)
H25	1.786192	0.654229	0.407446	0.049*
C26	1.6039 (8)	0.5251 (5)	0.3890 (3)	0.0406 (14)
C27	1.4381 (8)	0.4964 (5)	0.3909 (4)	0.0444 (15)
H27	1.395846	0.419088	0.377215	0.053*
C28	1.3330 (7)	0.5830 (4)	0.4133 (3)	0.0363 (13)
H28	1.219960	0.564316	0.415974	0.044*
C31	1.0349 (9)	1.1920 (5)	0.3835 (4)	0.0580 (17)
H31A	0.934264	1.164995	0.335747	0.087*
H31B	1.116213	1.232670	0.359985	0.087*
H31C	1.006659	1.243334	0.440846	0.087*

methanol (10 mL), [Ph₃(PhCH₂)P][Ru(acac)₂(CN)₂] $\cdot$ H₂O [5] (acac = acetylacetonato) (0.10 mmol, 72.2 mg) dissolved in methanol/water (4:1, v:v) (10 mL) was carefully added. The resulting mixture was filtered at once and the filtrate was kept undisturbed at room temperature for about one week. Then, the obtained title dark red block crystals were collected by filtration giving the yield of 77.2 mg (61.1%).

Experimental details

Coordinates of hydrogen atoms were assigned using geometrical constraints. Their *U*_{iso} values were set to 1.2*U*_{eq} or 1.5*U*_{eq} of the parent atoms.

Comment

Mn(III)-porphyrin compounds, containing Mn(III) ion with a large spin state (*S* = 2) and the typical Jahn–Teller elongation of the coordination octahedron, can induce large single ion magnetic axis anisotropy. They have been proven excellent candidates for synthesis of molecule-

based magnetic materials [6–10]. According to the previous report [5], the assembling of $[Mn(TPP)(H_2O)_2]ClO_4$ (TPP = 5,10,15,20-tetrakis(4-phenyl)porphyrinato) with *trans*-dicyanido-*k,N*-bis(acetylacetonato-*k_2O,O'*) ruthenium(III) could result in 1D cyanide-bridged Ru–Mn complexes exhibiting single chain magnet property, which enlighten us to further exploring Mn(III)-porphyrin based cyanide-bridged bimetallic magnetic complex.

The asymmetric unit of the title salt structure contains one half of $[Mn(TPP)(CH_3OH)_2]^+$ cation and one half of $[Ru(acac)_2(CN)_2]^-$ anion (see the figure). The coordination sphere for the Mn ion and the Ru(III) ion in the title complex can both be described as distorted octahedron, in which the four equatorial positions are occupied by four oxygen atoms of two acetylacetonato ions and four pyrrole N atoms, respectively, with the two axial ones resulting from two C atoms of cyano groups for Ru(III) ion and two O atoms of the methanol molecules for Mn(III) ion. The distances between Ru and the ligand O atoms are 1.998(4) and 2.007(3) Å, respectively, with the Ru–C distance of 2.079(6) Å, indicating the only slightly distorted octahedron around the Ru(III) ion. With comparison to the bond parameters around the Ru(III) ion, the equatorial Mn–N pyrrole bond lengths (2.014(3) and 2.023(4) Å) are obviously shorter than the Mn–O methanol bond length 2.307(3) Å, giving clear information about the elongated octahedral around the Mn(III) ion, typically accounting for the proverbial Jahn–Teller effect. Under the help of the intermolecular O–H...N (O...N = 2.788(6) Å) interactions between the O atom of the methanol molecule and the N atom of the cyanide group, the complex structure can be further discussed as a supramolecular chain structure.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: Shandong Provincial Natural Science Foundation (ZR2019BEM017 and ZR2019QB011)

and Weifang University Doctoral Research Funding (2019BS007).

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

References

1. Bruker. APEX2, SAINT-Plus, XPREP; Bruker AXS Inc.: Madison, Wisconsin, USA, 2004.
2. Sheldrick G. M. *SHELXTL* – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Zhang D. P., Wang H. L., Tian L. J., Kou H. Z., Jiang J. Z., Ni Z. H. Synthesis, crystal structures, and magnetic properties of cyanide-bridged Fe(III)–Mn(III) complexes based on manganese(III)-porphyrin and pyridinecarboxamide dicyanideiron(III) building blocks. *Cryst. Growth Des.* 2009, *9*, 3989–3996.
5. Zhang D. P., Zhang L. F., Chen Y. T., Wang H. L., Ni Z. H., Wernsdorfer W., Jiang J. Z. Heterobimetallic porphyrin-based single-chain magnet constructed from manganese(III)-porphyrin and *trans*-dicyanobis(acetylacetonato) ruthenate(III) containing co-crystallized bulk anions and cations. *Chem. Commun.* 2010, *46*, 3550–3552.
6. Bernot K., Luzon J., Sessoli R., Vindigni A., Thion J., Richeter S., Leclercq D., Larionova J., van der Lee A. The canted antiferromagnetic approach to single-chain magnets. *J. Am. Chem. Soc.* 2008, *130*, 1619–1627.
7. Rittenberg D. K., Sugiura K. I., Sakata Y., Mikami S., Epstein A. J., Miller J. S. Large coercivity and high remanent magnetization organic-based magnets. *Adv. Mater.* 2000, *12*, 126–130.
8. Zhang D. P., Lan W. L., Zhou Z., Yang L., Liu Q. Y., Bian Y. Z., Jiang J. Z. Manganese(III) porphyrin-based magnetic materials. *Top. Curr. Chem.* 2019, *377*, 18–60.
9. Zhang D. P., Zhao Z. D., Wang P., Ni Z. H. Substituent group tuned tri- and binuclear porphyrin based cyanide-bridged bimetallic complexes: synthesis, crystal structures and magnetic properties. *CrystEngComm* 2013, *15*, 2504–2511.
10. Chen X., Wu S. Q., Cui A. L., Kou H. Z. A cyano-bridged single-chain magnet featuring alternate high- and low-spin manganese(III) porphyrins. *Chem. Commun.* 2014, *50*, 2120–2122.