Kwang Ha*

Crystal structure of poly[tetra(μ_2 -cyanido- $\kappa^2N:O$)-bis(*N,N*-dimethylformamide- κO)-manganese(II)-platinum(II)], $C_{10}H_{14}MnN_6O_2Pt$

<https://doi.org/10.1515/ncrs-2021-0028>

Received January 17, 2021; accepted February 1, 2021;
published online February 11, 2021

Abstract

$C_{10}H_{14}MnN_6O_2Pt$, monoclinic, $C2/m$ (no. 12),
 $a = 15.8030(7)$ Å, $b = 7.6794(3)$ Å, $c = 7.0970(3)$ Å,
 $\beta = 110.8462(17)^\circ$, $V = 804.89(6)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0108$,
 $wR_{ref}(F^2) = 0.0266$, $T = 223$ K.

CCDC no.: 2060116

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

Source of material

To a yellow suspension of $[Mn(NCS)_2(bipy)_2]$ ($bipy = 2,2'$ -bipyridine; 0.2345 g; 0.485 mmol) in MeOH (30 mL) was added $K_2Pt(CN)_4$ (0.1830 g, 0.485 mmol) and stirred for 5 h at room temperature. The formed precipitate was

*Corresponding author: Kwang Ha, Research Institute of Catalysis, School of Chemical Engineering, Chonnam National University, Gwangju 61186, Republic of Korea, E-mail: hakwang@chonnam.ac.kr. <https://orcid.org/0000-0003-4628-2296>

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	$0.19 \times 0.18 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	9.47 mm^{-1}
Diffractometer, scan mode:	PHOTON 100 CMOS, φ and ω
$\theta_{\max}$, completeness:	26.1° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13,288, 857, 0.054
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 857
$N(\text{param})_{\text{refined}}$:	74
Programs:	BRUKER [1], SHELX [2], ORTEP-3 [3], PLATON [4]

separated by filtration, washed with MeOH, H₂O and acetone, and dried at 50 °C, to give a white powder (0.2274 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from an H₂O/*N,N*-dimethylformamide (DMF) solution at 60 °C.

Experimental details

All H atoms were located from Fourier difference maps and refined isotropically; C–H = 0.85(6)–1.01(4) Å. The highest peak (0.48 e Å^{−3}) and the deepest hole (−0.63 e Å^{−3}) in the difference Fourier map are located 0.88 and 0.87 Å from the atom Pt1, respectively.

Comment

The crystal structures of the related heterometallic cyanido-bridged Mn–Pt-complexes $[\{ Mn(\text{salen})_2Pt(CN)_4 \}]_n$ ($\text{salen} = N,N'$ -bis(salicylidene)ethylenediiminato) [5, 6], $[Mn(L)Pt(CN)_4]_n$ ($L = 2,13$ -dimethyl-3,12-diaza-6,9-dioxo-1(2,6)-pyridinacyclotridecaphane-2,12-diene) [7] and $[Mn(\text{phen})Pt(CN)_4]_n$ ($\text{phen} = 1,10$ -phenanthroline) [8] have been determined previously.

The title complex has a heterometallic polymeric structure, in which the cationic $[Mn(\text{DMF})]^{2+}$ (DMF = *N,N*-dimethylformamide) units are connected by the anionic

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
Pt1	0.0000	0.5000	1.0000	0.01293 (6)
Mn1	0.0000	0.0000	0.5000	0.01480 (13)
O1	0.13526 (15)	0.0000	0.4826 (4)	0.0309 (5)
N1	0.03721 (13)	0.2056 (2)	0.7346 (3)	0.0240 (4)
N2	0.23249 (18)	0.0000	0.3127 (5)	0.0307 (7)
C1	0.02585 (14)	0.3157 (3)	0.8325 (3)	0.0183 (4)
C2	0.1513 (2)	0.0000	0.3241 (5)	0.0272 (7)
H2	0.100 (2)	0.0000	0.190 (6)	0.029 (10)*
C3	0.2450 (3)	0.0000	0.1186 (7)	0.0529 (13)
H3A	0.300 (4)	0.0000	0.599 (9)	0.074 (19)*
H3B	0.284 (3)	0.100 (5)	0.122 (6)	0.075 (12)*
C4	0.3134 (3)	0.0000	0.4932 (9)	0.0592 (15)
H4A	0.185 (4)	0.0000	0.011 (9)	0.069 (17)*
H4B	0.354 (3)	0.089 (6)	0.484 (7)	0.108 (17)*

$[Pt(CN)_4]^{2-}$ bridges, forming a two-dimensional square-grid network. The linking of two Pt units and two Mn units forms a slightly puckered 12-membered square structure. In the complex, the Pt(II) ion is four-coordinated in a slightly distorted square-planar environment by four C atoms of four CN^- ligands, whereas the Mn(II) ion is six-coordinated in a slightly distorted octahedral environment by four N atoms from four bridging $[Pt(CN)_4]^{2-}$ units [9] and two axial O atoms from the two DMF solvent molecules, and the two metal cations are located on an inversion center, respectively. The complex is disposed about a twofold rotation axis running in the [010] direction passing through the Pt1 and Mn1 atoms, and has a crystallographic mirror plane parallel to the *ac* plane passing through the Pt1, Mn1, O1, N2, C2, C3 and C4 atoms, which are located at the special positions (*x*, 0, *z*), and thus the asymmetric unit contains one quarter of the compound [4]. The Mn–O axial bonds [Mn1–O1 = 2.185(2) Å] are slightly shorter than the Mn–N(cyanido) equatorial bonds [Mn1–N1 = 2.2170(18) Å].

Acknowledgements: The author thanks the KBSI, Seoul Center, for the X-ray data collection.

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

Research funding: This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (grant number: 2018R1D1A1B07050550)

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

References

1. Bruker. *APEX2, SAINT and SADABS*; Bruker AXS Inc.: Madison, WI, USA, 2016.
2. Sheldrick G. M. Crystal structure refinement with Shelxl. *Acta Crystallogr.* 2015, *C71*, 3–8.
3. Farrugia L. J. ORTEP-3 for Windows—a version of ORTEP-III with a graphical user interface (GUI). *J. Appl. Crystallogr.* 1997, *30*, 565.
4. Spek A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* 2003, *36*, 7–13.
5. Nemec I., Herchel R., Trávníček Z. Pentacoordinate and hexacoordinate Mn(III) complexes of tetradentate Schiff-base ligands containing tetracyanidoplatinate(II) bridges and revealing uniaxial magnetic anisotropy. *Molecules* 2016, *21*, 1681.
6. Ohtani R., Yamamoto R., Aoyama T., Grosjean A., Nakamura M., Clegg J. K., Hayami S. Positive and negative two-dimensional thermal expansion via relaxation of node distortions. *Inorg. Chem.* 2018, *57*, 11588–11596.
7. Bonadio F., Senna M.-C., Ensling J., Sieber A., Neels A., Stoeckli-Evans H., Decurtins S. Cyano-bridged structures based on $[Mn^{II}(N_3O_2\text{-macrocycle})]^{2+}$: a synthetic, structural, and magnetic study. *Inorg. Chem.* 2005, *44*, 969–978.
8. Hu A.-Y., Chen X., Chen Y.-Y., Zhou H., Yuan A.-H. Time-of-diffusion dependent structural diversity in the M^{II} -phen-tetracyanometalates ($M = Zn, Mn$) supramolecular system. *J. Mol. Struct.* 2013, *1037*, 301–304.
9. Zhang M., Li B.-B., Sun J., Kong X.-P., Gu P.-P., Chen Y.-Y., Yuan A.-H. Series of two-dimensional Hofmann–DMF-type compounds $M(DMF)_2(CN)_4$ ($M = Cd, Fe; = Ni, Pd, Pt$): syntheses, structures, and thermal stabilities. *Z. Anorg. Allg. Chem.* 2014, *640*, 1007–1011.