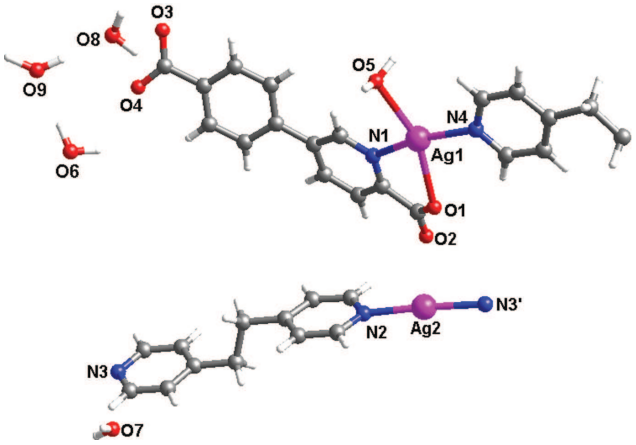
Hui-Tao Fan*, Jie Ding, Jing-Peng Xie and Kun Wang

Crystal structure of bis{*catena*-poly[(μ_2-1,2-bis(4-pyridyl)ethane-κ^2N:*N'*)silver(I)]} diaqua-bis(5-(4-carboxyphenyl)pyridine-2-carboxylato-κ^2N,*O*)-(μ_2-1,2-bis(4-pyridyl)ethane-κ^2N:*N'*)disilver(I) octahydrate, $C_{31}H_{35}Ag_2N_4O_9$



https://doi.org/10.1515/ncrs-2017-0345
Received January 4, 2018; accepted April 12, 2018; available online April 30, 2018

Abstract

$C_{31}H_{35}Ag_2N_4O_9$, triclinic, $P\bar{1}$ (No. 2), $a = 8.8351(5)$ Å, $b = 13.1492(6)$ Å, $c = 14.7094(8)$ Å, $V = 1618.76(15)$ Å^3, $\alpha = 85.491(4)$ Å, $\beta = 84.285(5)$ Å, $\gamma = 72.413(4)$ Å, $Z = 2$, $R_{gt}(F) = 0.0382$, $wR_{ref}(F^2) = 0.0796$, T = 293(2) K.

CCDC no.: 1586201

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

Excess aqueous NH_3 solution was slowly added dropwise to a suspension of Ag_2O (0.023 g, 0.1 mmol) in H_2O (6 mL), and the mixture was stirred for 30 min·H_2L (5-(4-carboxyphenyl)pyridine-2-carboxylic acid; 0.0122 g, 0.05 mmol), bpa (1,2-bis(4-pyridyl)ethane) (0.0184 g, 0.1 mmol) were then slowly added, and stirring was continued for another 30 min. The resultant colorless solution was allowed to stand in the dark at room temperature for a week. Colorless block crystals of the title complex were obtained.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.18 × 0.16 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.27 mm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, Gemini, φ and ω-scans
θ_{max}, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10674, 5698, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4546
$N(param)_{refined}$:	419
Programs:	CrysAlis^{PRO} [1], SHELX [2]

Experimental details

Absorption corrections were applied by using multi-scan program. Hydrogen atoms attached to C of the title complex located in difference electron density maps, and treated as riding atoms. The U_{iso} values of the hydrogen atoms of water molecules were set to $1.5U_{eq}$(O) and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{eq}$(C).

Comment

The metallophilic attractions are indeed present in all coinage metal ions (Cu(I), Ag(I), Au(I)), which have been confirmed by many studies [3–5]. Among them, the attractive interactions between the Ag centers, namely argentophilic interaction, have been used to form intriguing silver-organic frameworks with potential applications [6–9]. With the aim to expand our system [9] and construct unusual coordination architectures, we have engaged in the synthesis of coordination polymers based on H_2L (5-(4-carboxyphenyl)pyridine-2-carboxylic acid) with silver center.

Single crystal structure analysis reveals that the title structure consists of two crystallographically unique Ag(I) atoms, one L^{2-} ligand, one and a half bpa ligands, one

***Corresponding author: Hui-Tao Fan,** College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, China, e-mail: fanhuitao818@163.com
Jie Ding: College of Pharmacy, Henan Vocational College of Applied Technology, Kaifeng 475000, China
Jing-Peng Xie and Kun Wang: College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang 473061, China

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

Atom	x	y	z	U_{iso}*/U_{eq}
AG1	0.14446(4)	1.04441(2)	0.48144(2)	0.05172(11)
AG2	0.11176(4)	0.91201(2)	0.86438(2)	0.05760(12)
C1	0.4138(4)	0.9203(3)	0.6026(2)	0.0347(8)
C2	0.5596(5)	0.8558(3)	0.6274(3)	0.0422(9)
H2	0.590154	0.858156	0.685730	0.051*
C3	0.6603(4)	0.7877(3)	0.5658(3)	0.0406(9)
H3	0.758090	0.743311	0.582810	0.049*
C4	0.6157(4)	0.7853(3)	0.4782(2)	0.0338(8)
C5	0.4693(4)	0.8571(3)	0.4579(3)	0.0367(8)
H5	0.438285	0.859777	0.398915	0.044*
C6	0.7146(4)	0.7085(3)	0.4117(3)	0.0362(8)
C7	0.8138(4)	0.6105(3)	0.4424(3)	0.0466(10)
H7	0.818408	0.594570	0.504941	0.056*
C8	0.9049(4)	0.5366(3)	0.3825(3)	0.0464(10)
H8	0.968164	0.471338	0.405403	0.056*
C9	0.9045(4)	0.5573(3)	0.2894(3)	0.0380(9)
C10	0.8039(5)	0.6543(3)	0.2583(3)	0.0469(10)
H10	0.798977	0.669718	0.195645	0.056*
C11	0.7114(5)	0.7283(3)	0.3181(3)	0.0459(10)
H11	0.645699	0.792693	0.295121	0.055*
C12	0.2920(5)	0.9865(3)	0.6733(3)	0.0465(10)
C13	1.0100(4)	0.4750(3)	0.2249(3)	0.0435(10)
C14	0.4265(5)	0.7384(3)	0.8345(3)	0.0495(11)
H14	0.464926	0.797225	0.829721	0.059*
C15	0.5333(5)	0.6392(3)	0.8226(3)	0.0511(11)
H15	0.641121	0.631798	0.809382	0.061*
C16	0.4794(5)	0.5507(3)	0.8303(3)	0.0409(9)
C17	0.3192(5)	0.5671(3)	0.8503(3)	0.0463(10)
H17	0.278588	0.509205	0.856906	0.056*
C18	0.2183(5)	0.6689(3)	0.8607(3)	0.0491(10)
H18	0.109957	0.678113	0.873725	0.059*
C19	0.5918(5)	0.4391(3)	0.8200(3)	0.0492(10)
H19A	0.544338	0.398642	0.785225	0.059*
H19B	0.690414	0.442922	0.786481	0.059*
C20	0.6270(5)	0.3830(3)	0.9123(3)	0.0581(12)
H20A	0.528235	0.379660	0.945826	0.070*
H20B	0.674680	0.423522	0.946894	0.070*
C21	0.7390(5)	0.2710(3)	0.9029(3)	0.0479(10)
C22	0.8949(6)	0.2541(3)	0.8759(4)	0.0779(17)
H22	0.934813	0.311983	0.863720	0.093*
C23	0.9957(5)	0.1514(3)	0.8662(4)	0.0762(16)
H23	1.102141	0.142439	0.846785	0.091*
C24	0.7975(6)	0.0824(3)	0.9097(4)	0.0730(16)
H24	0.760417	0.023315	0.922347	0.088*
C25	0.6898(6)	0.1830(3)	0.9198(4)	0.0783(17)
H25	0.583551	0.189977	0.938318	0.094*
C26	−0.1352(5)	1.2283(3)	0.4012(3)	0.0578(12)
H26	−0.095845	1.191815	0.348089	0.069*
C27	−0.2631(6)	1.3149(3)	0.3961(4)	0.0691(14)
H27	−0.309380	1.336007	0.340967	0.083*
C28	−0.3241(5)	1.3710(3)	0.4702(4)	0.0628(14)
C29	−0.2529(6)	1.3366(4)	0.5505(4)	0.0746(16)
H29	−0.292729	1.373372	0.603336	0.089*
C30	−0.1174(5)	1.2441(3)	0.5522(3)	0.0625(12)
H30	−0.068672	1.221045	0.606448	0.075*
C31	−0.4738(7)	1.4738(4)	0.4578(3)	0.0783(15)
H31A	−0.445322	1.523072	0.411607	0.094*
H31B	−0.560147	1.452648	0.437005	0.094*
N1	0.3710(3)	0.9224(2)	0.5179(2)	0.0334(7)
N2	0.2700(4)	0.7546(2)	0.8528(2)	0.0448(8)
N3	0.9476(4)	0.0661(2)	0.8833(2)	0.0462(8)
N4	−0.0602(4)	1.1905(2)	0.4773(2)	0.0465(8)
O1	0.1546(4)	1.0273(3)	0.6536(2)	0.0717(9)
O2	0.3426(5)	0.9895(3)	0.7474(2)	0.0911(13)
O3	1.0182(3)	0.5026(2)	0.1416(2)	0.0567(8)
O4	1.0819(3)	0.3862(2)	0.2603(2)	0.0617(8)
O5	0.1648(4)	0.9865(3)	0.3185(2)	0.0763(10)
H5A	0.161786	1.047870	0.285096	0.092*
H5B	0.099816	0.950990	0.314706	0.092*
O6	0.1582(4)	0.1765(2)	0.2099(2)	0.0710(9)
H6A	0.132845	0.241209	0.224821	0.085*
H6B	0.207955	0.173369	0.154301	0.085*
O7[a]	0.482(3)	0.0671(17)	0.8524(16)	0.0990(17)
H7A[a]	0.537164	0.012456	0.878633	0.148*
H7B[a]	0.441574	0.046886	0.815753	0.148*
O7′[b]	0.4124(6)	0.0120(4)	0.9114(4)	0.0990(17)
H7C[b]	0.390615	0.005668	0.860093	0.148*
H7D[b]	0.488015	−0.034992	0.927053	0.148*
O8	0.1700(4)	0.3773(2)	−0.0019(2)	0.0829(11)
H8A	0.112517	0.415156	−0.046831	0.100*
H8B	0.121327	0.415436	0.043969	0.100*
O9	0.3070(5)	0.1648(3)	0.0305(3)	0.1074(15)
H9A	0.264655	0.232100	0.021482	0.129*
H9B	0.338155	0.119100	−0.005598	0.129*

Occupancies: [a] = 0.190(6), [b] = 0.810(6).

coordinated water molecule and four free water molecules. The central Ag1 cation coordinated to two nitrogen atoms from one L^{2-} ligand and one bpa ligand [Ag1—N1 = 2.237(2) and Ag1—N4 = 2.206(3) Å], and two oxygen atoms from one L^{2-} ligand and one coordinated water molecule [Ag1—O1 = 2.533(3) and Ag1—O5 = 2.545(3) Å]. The central Ag2 cation coordinated to two nitrogen atoms from two bpa ligands to generate $(Ag\text{-}bpa)_n$ chain with the distances of Ag—N 2.126(3) and 2.128(2) Å. Each bpa ligand as a bidentate ligand links Ag(I) centers and through Ag—Ag (Ag1—Ag1 3.099(5) Å) interactions to form infinite one-dimensional chain with the L^{2-} ligand on the two sides. Adjacent one-dimensional chains are linked through weak π-π-stacking interactions (3.360(2) Å) to give rise to layered structure parallel to the *bc* plane. Such layers are connected by Ag-bpa chain and water chain to form three-dimensional network through weak π-π-stacking interactions (3.473(2) Å) and hydrogen bonding.

Acknowledgements: We gratefully acknowledge the financial support by Scientific research and service platform fund

of Henan Province (2016151); The fund of scientific and technological innovation team of water ecological security for Water Source Region of Mid-line of South-to-North Diversion Project of Henan Province (17454), the National Natural Science Foundation of China (No. 21401112), the Science and Technology Research Key Project Department of Education in Henan Province (14 A150026) and Nanyang Normal University Scientific Research Foundation Project (QN2016015 and QN2017050).

References

1. Agilent Technologies.: CrysAlis^{PRO} Software system, version 1.171.38.41r, Agilent Technologies UK Ltd, Oxford, UK (2011).
2. Sheldrick, G. M.: Crystal structure refinement with *SHELXL*. Acta Crystallogr. **C71** (2015) 3–8.
3. Veselska, O.; Okhrimenko, L.; Guillou, N.; Podbevsek, D.; Ledoux, G.; Dujardin, C.; Monge, M.; Chevrier, D. M.; Yang, R.; Zhang, P.; Fateeva, A.; Demessence A.: An intrinsic dual-emitting gold thiolate coordination polymer, $[Au(+I)(p\text{-}SPhCO_2H)]_n$, for ratiometric temperature sensing. J. Mater. Chem. **C5** (2017) 9843–9848.
4. Lim, M. J.; Murray, C. A.; Tronic, T. A.; deKrafft, K. E.; Ley, A. N.; deButts, J. C.; Pike, R. D.; Lu, H. Y.; Patterson, H. H.: Copper(I) cyanide networks: synthesis, structure, and luminescence behavior. Part 2. Piperazine ligands and hexamethylenetetramine. Inorg. Chem. **47** (2008) 6931–6947.
5. Li, B.; Huang, R. W.; Qin, J. H.; Zang, S. Q.; Gao, G. G.; Hou, H. W.; Mak, T. C. W.: Thermochromic luminescent nest-like silver thiolate cluster. Chem. Eur. J. **20** (2014) 12416–12420.
6. Yuan, S.; Deng, Y. K.; Wang, X. P.; Sun, D.: A temperature-sensitive luminescent Ag_{20} nanocluster template by carbonate in situ generated from atmospheric CO_2 fixation. New J. Chem. **37** (2013) 2973–2977.
7. Sun, D.; Wang, H.; Lu, H. F.; Feng, S. Y.; Zhang, Z. W.; Sun, G. X.; Sun, D. F.: Two birds with one stone: anion templated ball-shaped Ag_{56} and disc like Ag_{20} clusters. Dalton Trans. **42** (2013) 6281–6284.
8. Xu, Q. Q.; Dong, X. Y.; Huang, R. W.; Li, B.; Zang, S. Q.; Mak, T. C. W.: A thermochromic silver nanocluster exhibiting dual emission character. Nanoscale **7** (2015) 1650–1654.
9. Fan, H. T.; Zhong, Z. G.; Yang, Y. H.; Zhao, L.: Crystal structure of ([3,3′-bipyridine]-6,6′-dicarboxylato-κ^2*O:O′*)-bis(1,2-bis(4-pyridyl)ethane-κ^2*N:N′*)disilver(I) dihydrate, $C_{37}H_{35}Ag_2N_5O_6$. Z. Kristallogr. NCS **232** (2017) 587–589.