Crystal structure of *meso*-5,5,7,12,12,14-hexamethyl-4,11-diaza-1,8-diazoniacyclotetradecane bis(dicyanoargentate) dihydrate, $(C_{16}H_{38}N_4)[Ag(CN)_2]_2 \cdot 2H_2O$

J.-G. Ding*

Suzhou University, College of Chemistry and Chemical Engineering, Suzhou, 215123 P. R. China

Received September 13, 2005, accepted and available on-line December 3, 2005; CCDC no. 1267/1646

Abstract

$C_{20}H_{42}Ag_2N_8O_2$, monoclinic, $P1n1$ (no. 7), $a = 12.061(3)$ Å, $b = 7.704(2)$ Å, $c = 14.734(4)$ Å, $\beta = 90.022(6)^\circ$, $V = 1369.1$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.029$, $wR_{\text{ref}}(F^2) = 0.069$, $T = 193$ K.

Source of material

meso-5,5,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane (teta) was prepared according to a literature method [1]. 5 ml aqueous solution of $K[Ag(CN)_2]$ (0.080 g, 0.4 mmol) was added slowly to 5 ml methanolic solution of $teta \cdot 2H_2O$ (0.064 g, 0.2 mmol). The resulted solution was continuously stirred for 30 min and then filtered. Colorless block-like single crystals were obtained after ten days.

Experimental details

H atoms bonded to C atoms were positioned geometrically and treated as riding. The H atoms attached to O or N atoms were located from Fourier difference maps and refined with restraints for O—H and N—H distances (0.92(2) Å).

Discussion

The compound consists of one protonated macrocyclic tetraamine cation, $[H_2(teta)]^{2+}$, two $[Ag(CN)_2]^-$ anions and two water molecules. In the $[Ag(CN)_2]^-$ anions, the Ag(I) ions are coordi-

nated each to two carbon atoms of cyano groups in a nearly linear environment with bond angles of C—Ag—C of $177.4(1)^\circ$ and $175.8(1)^\circ$. The Ag—C bond lengths are almost equivalent falling in the ranges of $2.048(4)$ Å – $2.060(3)$ Å. The macrocyclic tetraamine cation contains two protonated secondary amine N atoms (N1, N3) and two secondary amine N atoms (N2, N4). The N—C and C—C bond lengths are very similar to those of $[H_2(teta)]^{2+}(ClO_4^-)_2 \cdot H_2O$ [2] and $[H_2(teta)]^{2+}(SCN^-)_2$ [3]. There are multiform hydrogen bonds in the compound. Inside the macrocyclic tetraamine cation $[H_2(teta)]^{2+}$, each protonated amine N atom forms an intramolecular hydrogen bond with the second amine N atom (N1—H1D...N2, $d(N1...N2) = 2.798(3)$ Å; N3—H3D...N4, $d(N3...N4) = 2.839(4)$ Å). There are also hydrogen bonds between the amine N atoms and water molecules (N1—H1E...O2, $d(N1...O2) = 2.740(3)$ Å; N3—H3E...O1, $d(N3...O1) = 3.125(4)$ Å; N4—H4D...O1, $d(N4...O1) = 3.066(4)$ Å), among the amine N atoms and the cyano N atoms of $[Ag(CN)_2]^-$ (N2—H2D...N8, $d(N2...N8) = 3.282(4)$ Å; N3—H3E...O1, $d(N3...O1) = 3.125(4)$ Å). Moreover, hydrogen bonds are formed among the water molecules and cyano N atoms (O1—HW1...N6, $d(O1...N6) = 3.008(4)$ Å; O1—HW2...N7ⁱ, $d(O1...N7) = 2.817(5)$ Å; O2—HW3...N8, $d(O2...N8) = 2.885(4)$ Å; O2—HW4...N5ⁱⁱ, $d(O2...N5) = 2.850(4)$ Å, symmetry codes: (i) $1+x, -1+y, z$; (ii) $x, 1+y, -1+z$). Therefore, a series of these hydrogen bonds and the static force connect three components of the compound and maintain the crystal structure. The Flack x parameter had a value of 0.45(2).

Table 1. Data collection and handling.

Crystal:	colorless block, size $0.24 \times 0.30 \times 0.55$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	14.61 cm^{-1}
Diffractionmeter, scan mode:	Rigaku AFC-8 & Mercury CCD, ω
$2\theta_{\text{max}}$:	54.96°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	14772, 5812
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5340
$N(\text{param})_{\text{refined}}$:	328
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
HW(1)	2a	0.831(3)	0.422(6)	0.637(2)	0.06(1)
HW(2)	2a	0.929(2)	0.437(7)	0.575(4)	0.10(2)
HW(3)	2a	0.680(2)	1.023(5)	0.356(3)	0.04(1)
HW(4)	2a	0.746(4)	1.066(6)	0.277(2)	0.07(2)
H(1D)	2a	0.803(3)	0.695(4)	0.431(2)	0.04(1)
H(1E)	2a	0.819(3)	0.834(3)	0.366(3)	0.04(1)

* e-mail: uudg1688@public1.sz.js.cn

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(2D)	2a	0.603(2)	0.730(3)	0.425(2)	0.022(8)
H(3D)	2a	0.734(2)	0.761(5)	0.584(2)	0.035(9)
H(3E)	2a	0.708(3)	0.662(3)	0.664(2)	0.034(9)
H(4D)	2a	0.922(4)	0.759(4)	0.592(3)	0.06(1)
H(1A)	2a	0.9752	0.6789	0.2340	0.064
H(1B)	2a	0.8651	0.7832	0.2076	0.064
H(1C)	2a	0.8836	0.5900	0.1707	0.064
H(3A)	2a	0.9682	0.4423	0.3485	0.059
H(3B)	2a	0.8793	0.3379	0.2891	0.059
H(3C)	2a	0.8524	0.3858	0.3925	0.059
H(4A)	2a	0.6857	0.6957	0.2693	0.037
H(4B)	2a	0.7046	0.5033	0.2332	0.037
H(5A)	2a	0.6666	0.3951	0.3824	0.035
H(6A)	2a	0.4723	0.4344	0.3691	0.060
H(6B)	2a	0.5260	0.3976	0.2716	0.060
H(6C)	2a	0.4919	0.5911	0.2996	0.060
H(7A)	2a	0.6223	0.4616	0.5449	0.038
H(7B)	2a	0.5052	0.5199	0.5034	0.038

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(8A)	2a	0.5328	0.8026	0.5667	0.038
H(8B)	2a	0.5234	0.6551	0.6429	0.038
H(9A)	2a	0.5376	0.8807	0.7503	0.066
H(9B)	2a	0.6226	0.9963	0.8078	0.066
H(9C)	2a	0.6386	0.7903	0.8026	0.066
H(11A)	2a	0.5710	1.0501	0.6096	0.060
H(11B)	2a	0.6944	1.0756	0.5719	0.060
H(11C)	2a	0.6555	1.1759	0.6615	0.060
H(12A)	2a	0.8137	1.0230	0.7618	0.037
H(12B)	2a	0.8345	0.8233	0.7394	0.037
H(13A)	2a	0.8694	1.0999	0.6135	0.034
H(14A)	2a	1.0614	1.0445	0.6360	0.065
H(14B)	2a	1.0315	0.9040	0.7121	0.065
H(14C)	2a	1.0037	1.1046	0.7286	0.065
H(15A)	2a	1.0379	0.9284	0.5088	0.038
H(15B)	2a	0.9313	1.0115	0.4605	0.038
H(16A)	2a	1.0121	0.7901	0.3681	0.037
H(16B)	2a	0.9906	0.6513	0.4472	0.037

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ag(1)	2a	0.75721(1)	0.31086(4)	0.95636(1)	0.0372(2)	0.0579(2)	0.0308(2)	-0.0039(1)	-0.0013(1)	0.0043(1)
Ag(2)	2a	0.30151(2)	1.18723(3)	0.48229(2)	0.0358(2)	0.0576(2)	0.0391(2)	0.0033(1)	0.0022(1)	0.0050(1)
O(1)	2a	0.8563(3)	0.4638(4)	0.5836(2)	0.058(2)	0.047(2)	0.079(2)	0.016(2)	0.029(2)	0.017(2)
O(2)	2a	0.7482(2)	1.0329(3)	0.3354(2)	0.041(1)	0.042(1)	0.042(1)	0.002(1)	0.002(1)	0.012(1)
N(1)	2a	0.8488(2)	0.7272(3)	0.3830(2)	0.023(1)	0.027(1)	0.026(1)	-0.000(1)	0.002(1)	-0.001(1)
N(2)	2a	0.6365(2)	0.6299(3)	0.4401(2)	0.027(1)	0.021(1)	0.029(1)	-0.002(1)	0.001(1)	0.000(1)
N(3)	2a	0.6811(2)	0.7500(3)	0.6286(2)	0.028(1)	0.025(1)	0.024(1)	0.001(1)	0.001(1)	-0.001(1)
N(4)	2a	0.8932(2)	0.8562(3)	0.5662(2)	0.030(1)	0.025(1)	0.026(1)	-0.004(1)	-0.002(1)	0.000(1)
N(5)	2a	0.7886(3)	0.1518(4)	1.1553(2)	0.059(2)	0.057(2)	0.039(2)	-0.008(2)	-0.000(2)	0.005(1)
N(6)	2a	0.7218(3)	0.4584(4)	0.7554(2)	0.050(2)	0.046(2)	0.038(2)	0.002(1)	-0.002(1)	0.003(1)
N(7)	2a	0.0759(3)	1.3764(5)	0.5370(2)	0.050(2)	0.061(2)	0.065(2)	0.014(2)	0.010(2)	0.017(2)
N(8)	2a	0.5295(3)	1.0185(5)	0.4142(2)	0.052(2)	0.069(2)	0.038(2)	0.016(2)	0.001(2)	0.007(1)
C(1)	2a	0.8956(3)	0.6686(5)	0.2220(2)	0.042(2)	0.058(2)	0.028(2)	-0.000(2)	0.010(1)	-0.005(1)
C(2)	2a	0.8375(3)	0.5962(4)	0.3062(2)	0.032(2)	0.033(2)	0.026(2)	0.002(1)	0.004(1)	-0.007(1)
C(3)	2a	0.8889(3)	0.4253(4)	0.3368(3)	0.036(2)	0.035(2)	0.047(2)	0.005(1)	-0.002(2)	-0.007(1)
C(4)	2a	0.7133(2)	0.5795(4)	0.2868(2)	0.029(2)	0.038(2)	0.026(2)	-0.000(1)	-0.000(1)	-0.008(1)
C(5)	2a	0.6369(3)	0.5096(4)	0.3617(2)	0.030(2)	0.027(1)	0.031(2)	0.001(1)	-0.004(1)	-0.002(1)
C(6)	2a	0.5214(3)	0.4806(4)	0.3219(2)	0.037(2)	0.042(2)	0.041(2)	-0.009(1)	-0.006(2)	-0.005(2)
C(7)	2a	0.5800(2)	0.5614(4)	0.5205(2)	0.030(2)	0.035(2)	0.032(2)	-0.009(1)	0.003(1)	0.000(1)
C(8)	2a	0.5699(2)	0.6992(3)	0.5926(2)	0.023(2)	0.042(2)	0.029(2)	-0.003(1)	0.003(1)	-0.002(1)
C(9)	2a	0.6152(2)	0.8937(3)	0.7689(2)	0.046(2)	0.049(2)	0.037(2)	0.004(2)	0.009(2)	-0.013(2)
C(10)	2a	0.6881(3)	0.9154(4)	0.6849(2)	0.034(2)	0.028(2)	0.027(2)	0.004(1)	0.000(1)	-0.006(1)
C(11)	2a	0.6487(3)	1.0679(4)	0.6267(2)	0.048(2)	0.029(2)	0.043(2)	0.006(2)	-0.007(2)	-0.003(1)
C(12)	2a	0.8100(3)	0.9350(4)	0.7129(2)	0.040(2)	0.025(1)	0.027(2)	-0.000(1)	-0.003(1)	-0.003(1)
C(13)	2a	0.8935(3)	0.9863(4)	0.6399(2)	0.033(2)	0.025(1)	0.027(2)	-0.006(1)	-0.005(1)	-0.004(1)
C(14)	2a	1.0078(3)	1.0122(5)	0.6830(2)	0.043(2)	0.051(2)	0.036(2)	-0.014(2)	-0.009(2)	-0.006(2)
C(15)	2a	0.9612(3)	0.9045(4)	0.4885(2)	0.031(2)	0.032(2)	0.032(2)	-0.009(1)	-0.002(1)	-0.003(1)
C(16)	2a	0.9620(2)	0.7588(4)	0.4188(2)	0.023(1)	0.037(2)	0.032(2)	-0.004(1)	0.003(1)	-0.001(1)
C(17)	2a	0.7786(3)	0.2097(5)	1.0844(3)	0.037(2)	0.053(2)	0.036(2)	-0.005(2)	0.002(2)	-0.002(2)
C(18)	2a	0.7346(3)	0.4010(4)	0.8261(2)	0.034(2)	0.037(2)	0.036(2)	-0.001(1)	-0.000(1)	-0.002(1)
C(19)	2a	0.1574(3)	1.3096(5)	0.5182(3)	0.038(2)	0.051(2)	0.051(2)	-0.001(2)	0.001(2)	0.016(2)
C(20)	2a	0.4477(3)	1.0774(5)	0.4388(2)	0.046(2)	0.054(2)	0.034(2)	0.001(2)	-0.001(2)	0.010(2)

Acknowledgment. The authors is indebted to Mr. Yong Zhang for X-ray data collection.

References

- Robert, W. H.; Geoffrey, A. L.; Curtis, N. F.: Convenient synthesis of the tetra-aza-macrocyclic ligands *trans*-[14]-diene, tet a and tet b. *J. Chem. Soc., Perkin Trans. I* (1975) 591-593.
- Hu, H.; Sun, H.; Huang, X.: *Meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane dihydroperchlorate monohydrate. *Acta Crystallogr. C53* (1997) 588-590.
- Drew, G. B. M.; Mok, K.: A dihydrothiocyanate of a 14-membered tetra-aza macrocycle. *Acta Crystallogr. C43* (1987) 773-775.
- Sheldrick, G. M.: Phase annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr. A46* (1990) 467-473.
- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.