Crystal structure of diethylenetriammonium silver(I) di(4-nitrobenzoate) monohydrate, $[\text{Ag}(\text{C}_4\text{H}_{14}\text{N}_3)](\text{C}_7\text{H}_4\text{NO}_4)_2 \cdot \text{H}_2\text{O}$

H.-L. Zhu^{*,I,II}, S.-C. Shao^I, S. Yang^I, X.-Y. Qiu^I, J.-L. Ma^I and H.-K. Fun^{III}

^I Fuyang Normal College, Department of Chemistry, Fuyang, Anhui, 236041 P. R. China

^{II} Wuhan University of Science and Engineering, Department of Chemistry, Wuhan, 430073 P. R. China

^{III} Universiti Sains Malaysia, School of Physics, X-Ray Crystallography Unit, 11800 USM, Penang, Malaysia

Received September 10, 2003; accepted and available on-line November 15, 2003; CCDC-No. 1267/1149

Abstract

$\text{C}_{18}\text{H}_{24}\text{AgN}_5\text{O}_9$, monoclinic, $P12_1/n1$ (No. 14), $a = 6.2181(3) \text{ \AA}$, $b = 26.975(2) \text{ \AA}$, $c = 13.1982(7) \text{ \AA}$, $\beta = 99.648(2)^\circ$, $V = 2182.5 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.038$, $wR_{\text{ref}}(F^2) = 0.082$, $T = 293 \text{ K}$.

Source of material

Reagents and solvents used were of commercially available reagent quality. As described in our previous paper [1], 4-(NO_2)(C_6H_4)COOH (1 mmol, 0.17 g) and Ag_2O (0.5 mmol, 0.12 g) were dissolved in 30% ammonium solution (10 ml), diethylenetriamine (1 mmol, 103 mg) was added with stirring for 1 h. Crystals were formed after the filtrate was stood still in air for two days. The colorless crystals were filtrated and washed with ammonium solution and water, respectively, and dried in air (yield 93%). Elemental analysis: found – C, 38.21%; H, 4.24%; N, 12.39%; calc. for $\text{C}_{18}\text{H}_{24}\text{AgN}_5\text{O}_9$ – C, 38.45%; H, 4.30%; N, 12.46%.

Experimental details

All the H-atoms were located from Fourier maps and were refined isotropically. They were constrained to ride on their parent atoms with N–H and C–H distances of 0.90 Å and 0.96 Å, respectively.

Discussion

Recently, we systematically reported [1] the synthesis and property of diethylenetriaminesilver(I) complexes containing various counter anions. As a continuation, we prepared and structurally

characterized the crystal structure of the title complex. One primary amine N atom in dien was protonized, so the protonized dienH^+ acted as a bidentate bridging ligand. The nice crystals of the title compound are not very stable and change to a white powder when kept in a vacuum desiccator at room temperature for more than one day. The elemental analysis data and IR spectrum showed that the white powder was the same as the compound reported previously in [1]. Reported in this paper is a polymeric diethylenetriammonium silver(I) complex.

In the structure of the title compound each simplest repeating unit consists of a diethylenetriammonium silver(I) dication, two 4-nitrobenzoate anions, and a lattice water molecule. In the cation, the central silver(I) atom is coordinated by two nitrogen atoms from different diethylenetriamine molecules at the distance of $\text{Ag}(1)\text{—N}(2) = 2.171(2) \text{ \AA}$ and $\text{Ag}(1)\text{—N}(1A) = 2.150(2) \text{ \AA}$. The N–Ag–N angle is close to 180° ($174.32(9)^\circ$), indicating a slightly distorted environment of Ag(1). One of the three nitrogen atoms in the dien ligand is protonated, namely N(3). The dien acts as a bidentate ligands by N(1) and N(2) atoms ligating to different silver(I) atoms. The one-dimensional chain [Ag(dien)] stretches along a -axis. The 4-nitrobenzoates locate at different sides of the 1D chain, and the two aromatic rings are nearly parallel to each other with the dihedral angle of $4.40(2)^\circ$. A great number of hydrogen bonds join the complex to form a three-dimensional network.

* Correspondence author (e-mail: hlzhu@wist.edu.cn)

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.22 × 0.26 × 0.50 mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	9.85 cm ⁻¹
Diffractionmeter, scan mode:	Siemens SMART CCD, ω
$2\theta_{\max}$:	56.6°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	13779, 5366
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > \sigma(I_{\text{obs}})$, 4632
$N(\text{param})_{\text{refined}}$:	394
Programs:	SHELXTL [2], SHELXTL-plus [3]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4e	0.707(4)	0.218(1)	0.321(2)	0.032(7)
H(1B)	4e	0.556(5)	0.204(1)	0.225(2)	0.041(8)
H(2A)	4e	0.792(5)	0.132(1)	0.344(2)	0.041(8)
H(2B)	4e	0.623(4)	0.122(1)	0.249(2)	0.033(7)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(3A)	4e	0.599(5)	0.082(1)	0.450(2)	0.043(8)
H(3B)	4e	0.436(5)	0.069(1)	0.358(3)	0.049(9)
H(4A)	4e	0.301(6)	0.118(1)	0.527(3)	0.06(1)
H(4B)	4e	0.142(7)	0.100(2)	0.433(3)	0.08(1)
H(6)	4e	-0.667(5)	0.151(1)	-0.209(2)	0.035(7)
H(7)	4e	-0.933(5)	0.159(1)	-0.349(2)	0.036(7)
H(9)	4e	-1.346(5)	0.220(1)	-0.185(2)	0.036(7)
H(10)	4e	-1.089(5)	0.214(1)	-0.035(2)	0.050(9)
H(13)	4e	0.661(6)	0.077(1)	0.851(3)	0.06(1)
H(14)	4e	0.821(5)	0.087(1)	1.015(2)	0.044(8)
H(16)	4e	1.368(6)	0.030(1)	0.947(3)	0.06(1)
H(17)	4e	1.207(5)	0.019(1)	0.779(2)	0.040(8)
H(1N1)	4e	0.879(5)	0.227(1)	0.184(2)	0.045(9)
H(2N1)	4e	0.823(6)	0.181(1)	0.151(3)	0.05(1)
H(1N2)	4e	0.509(5)	0.158(1)	0.407(2)	0.037(9)
H(1N3)	4e	0.395(8)	0.039(2)	0.573(4)	0.10(2)
H(2N3)	4e	0.136(6)	0.043(1)	0.557(3)	0.06(1)
H(3N3)	4e	0.227(5)	0.018(1)	0.474(2)	0.037(8)
H(1W1)	4e	0.002(6)	0.206(1)	0.494(3)	0.05(1)

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)	4e	0.16889(3)	0.172472(8)	0.28610(2)	0.0226(1)	0.0489(1)	0.0464(1)	0.00378(8)	0.00699(8)	0.01326(9)
O(1)	4e	-0.7493(5)	0.1867(1)	0.0661(2)	0.070(2)	0.128(2)	0.029(1)	0.015(2)	0.001(1)	0.006(1)
O(2)	4e	-0.5175(4)	0.1578(1)	-0.0215(2)	0.043(1)	0.081(2)	0.056(1)	0.008(1)	-0.006(1)	0.006(1)
O(3)	4e	-1.2707(3)	0.18591(9)	-0.4645(2)	0.035(1)	0.093(2)	0.031(1)	-0.005(1)	0.0035(8)	-0.015(1)
O(4)	4e	-1.5257(3)	0.20515(8)	-0.3715(2)	0.0274(9)	0.064(1)	0.041(1)	0.0008(9)	0.0021(8)	-0.0075(9)
O(5)	4e	0.9035(4)	0.02770(9)	0.6206(2)	0.051(1)	0.081(2)	0.039(1)	-0.021(1)	0.0131(9)	-0.013(1)
O(6)	4e	0.5926(4)	0.0406(1)	0.6761(2)	0.035(1)	0.130(2)	0.043(1)	-0.005(1)	-0.0069(9)	0.001(1)
O(7)	4e	1.1134(6)	0.0782(1)	1.1678(2)	0.152(3)	0.075(2)	0.042(1)	-0.013(2)	-0.002(2)	-0.016(1)
O(8)	4e	1.4171(6)	0.0526(1)	1.1263(2)	0.103(2)	0.086(2)	0.071(2)	-0.006(2)	-0.047(2)	0.000(2)
N(1)	4e	0.8597(3)	0.1963(1)	0.2022(2)	0.029(1)	0.042(1)	0.030(1)	-0.0041(9)	0.0045(9)	0.004(1)
N(2)	4e	0.4753(3)	0.14141(8)	0.3629(2)	0.025(1)	0.034(1)	0.029(1)	-0.0029(8)	0.0045(8)	-0.0017(9)
N(3)	4e	0.2597(4)	0.04386(9)	0.5234(2)	0.032(1)	0.046(1)	0.032(1)	-0.006(1)	0.0045(9)	0.004(1)
N(4)	4e	-0.6953(4)	0.17509(9)	-0.0152(2)	0.042(1)	0.046(1)	0.037(1)	-0.006(1)	-0.000(1)	0.011(1)
N(5)	4e	1.2240(7)	0.0639(1)	1.1052(2)	0.105(3)	0.039(2)	0.046(2)	-0.019(2)	-0.019(2)	0.002(1)
C(1)	4e	0.6802(4)	0.1947(1)	0.2621(2)	0.022(1)	0.037(1)	0.034(1)	0.003(1)	0.005(1)	0.003(1)
C(2)	4e	0.6508(4)	0.14307(9)	0.3010(2)	0.024(1)	0.034(1)	0.034(1)	-0.0009(9)	0.008(1)	-0.002(1)
C(3)	4e	0.4552(4)	0.0919(1)	0.4076(2)	0.030(1)	0.038(1)	0.036(1)	-0.001(1)	0.005(1)	0.004(1)
C(4)	4e	0.2739(5)	0.0922(1)	0.4718(3)	0.034(2)	0.046(2)	0.053(2)	0.002(1)	0.013(1)	0.013(1)
C(5)	4e	-0.8580(4)	0.18085(9)	-0.1093(2)	0.034(1)	0.033(1)	0.030(1)	-0.005(1)	0.003(1)	0.007(1)
C(6)	4e	-0.8065(4)	0.1642(1)	-0.2011(2)	0.029(1)	0.042(2)	0.037(1)	0.002(1)	0.008(1)	0.003(1)
C(7)	4e	-0.9631(4)	0.1688(1)	-0.2885(2)	0.035(1)	0.041(1)	0.030(1)	0.001(1)	0.009(1)	-0.004(1)
C(8)	4e	-1.1661(4)	0.18926(9)	-0.2842(2)	0.031(1)	0.031(1)	0.029(1)	-0.0062(9)	0.0062(9)	-0.0022(9)
C(9)	4e	-1.2111(4)	0.20565(9)	-0.1895(2)	0.031(1)	0.036(1)	0.032(1)	0.001(1)	0.009(1)	-0.002(1)
C(10)	4e	-1.0572(4)	0.2021(1)	-0.1017(2)	0.042(2)	0.039(1)	0.026(1)	-0.000(1)	0.008(1)	0.000(1)
C(11)	4e	-1.3350(4)	0.1940(1)	-0.3810(2)	0.029(1)	0.038(1)	0.031(1)	-0.007(1)	0.004(1)	-0.005(1)
C(12)	4e	0.9139(4)	0.04744(9)	0.7973(2)	0.032(1)	0.036(1)	0.032(1)	-0.007(1)	0.002(1)	0.002(1)
C(13)	4e	0.8015(5)	0.0677(1)	0.8698(2)	0.040(2)	0.043(2)	0.043(2)	0.001(1)	0.006(1)	0.002(1)
C(14)	4e	0.9021(6)	0.0736(1)	0.9708(2)	0.064(2)	0.041(2)	0.037(2)	-0.002(1)	0.010(1)	-0.007(1)
C(15)	4e	1.1158(5)	0.0595(1)	0.9963(2)	0.062(2)	0.031(1)	0.034(1)	-0.011(1)	-0.010(1)	0.002(1)
C(16)	4e	1.2328(5)	0.0401(1)	0.9263(2)	0.038(2)	0.047(2)	0.050(2)	-0.002(1)	-0.010(1)	0.009(1)
C(17)	4e	1.1303(5)	0.0344(1)	0.8260(2)	0.038(2)	0.043(2)	0.043(2)	-0.001(1)	0.004(1)	-0.002(1)
C(18)	4e	0.7938(5)	0.0386(1)	0.6892(2)	0.041(2)	0.051(2)	0.032(1)	-0.011(1)	0.001(1)	0.003(1)
O(1W)	4e	0.1093(4)	0.2159(1)	0.4694(2)	0.046(1)	0.084(2)	0.040(1)	-0.007(1)	0.010(1)	0.010(1)

Acknowledgments. The authors thank the Education Office of Hubei Province P. R. China (grant No. 2002B29002) and the Natural Science Foundation of Hubei Province P. R. China (grant No. 2003ABB010).

References

- Zhu, H.-L.; Wang, X.-J.; Liu X.-Y.; Wang, D.-Q.: Synthesis and Characterization of Ag(I) Salts with Diethylenetriamine. Crystal structure of [Ag₂(dien)₂](ClO₄)₂. Synth. React. Inorg., Met-Org. Chem. **33** (2003) 1417-1424.
- Sheldrick, G. M.: Siemens SHELXTL (Version 5.0): Siemens Industrial Automation, Inc., analytical Instrumentation, USA 1995.
- Sheldrick, G. M.: SHELXTL-plus. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison Wisconsin, USA 1991.