Inorg. Chem. **1998,** *37,* 2605−2607 **2605**

An Octacationic Carboxylate−Silver(I) Cluster Complex

Pingrong Wei,[†] Thomas C. W. Mak,[‡] and
David A. Atwood*,[†]

Center for Main Group Chemistry, Department of Chemistry,
North Dakota State University, Fargo, North Dakota 58105,
and Department of Chemistry, The Chinese University of
Hong Kong, Shatin, New Territories, Hong Kong

Received October 10, 1997

Introduction

The isolation of silver (I) carboxylate complexes is complicated by the fact that they are generally light sensitive.[1] Stable, soluble complexes can, however, be isolated by the use of various "betaine" ligands (Figure 1).[2] Soluble transition metal complexes can be obtained in a similar manner.[3] Structural characterization of several silver−betaine complexes has revealed a diverse bonding arrangement for the silver atoms. The carboxylate groups can adopt four general bonding modes (Figure 2). Often, the silver atoms organize into dimeric and trimeric subunits. In the present study, a new silver−betaine complex will be described. It is remarkable in that it is made up of two dissimilar unsymmetrical pentasilver clusters connected by μ_2-bridging of one carboxylate ligand.

Results and Discussion

Compound **1** is formed in distilled water by combining Ag(OTf) (OTf = CF_3SO_3) with the betaine ligand (Figure 1(II)). High yields of X-ray-quality crystals are obtained by crystallization of the compound in air. It forms as a 10-atom cationic cluster held together by bridging carboxylate groups (Figure 3). The clusters possess an overall 8+ charge and are arranged in stacks with all of the pyridine rings of the ligand oriented in a coplanar fashion. The eight OTf^- groups occupy the space between the clusters along with four waters of crystallization. The remaining two OTf^- groups form η^1 bonds to silver atoms (Ag4 and Ag9); the remaining four waters fill an Ag coordination site (Ag2, Ag3, Ag6, and Ag10).

The 10-atom cluster can be subdivided into two five-atom clusters linked by a type C carboxylate group (Figure 4). There are two types of five-atom clusters with contacts within the sum of the van der Waals radii of Ag (1.7 Å) (Table 2). In one, there is a four-atom butterfly cluster (Ag6−Ag9) containing an appended Ag atom (Ag10). Within the four atoms, the Ag−Ag distances are ~3.0 Å except for those to Ag9, which are ~3.3 Å. The Ag atoms at the vertexes (Ag6 and Ag9) are five- and six-coordinate, respectively, and interconnected by μ_2-(type A) carboxylates. Another type C carboxylate connects this group of Ag atoms to the second with an Ag−O distance of 2.308(9) Å.

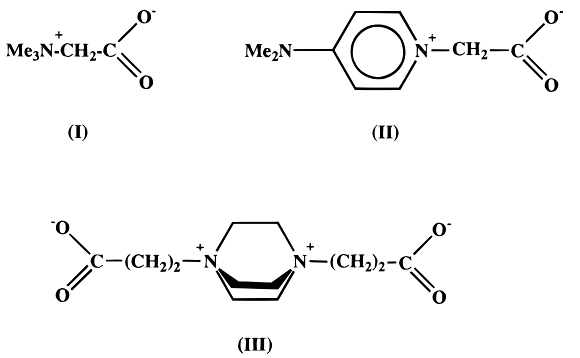

Figure 1. Various betaine ligands that are useful in creating Ag(I) and transition metal complexes that are soluble in water.

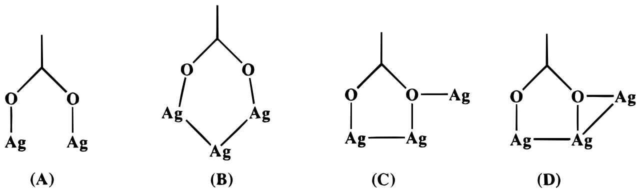

Figure 2. The three types of carboxylate groups in compound **1**.

Table 1. Crystal Data for Compound **1**

formula	$C_{118}H_{160}Ag_{10}F_{30}N_{24}O_{62}S_{10}$
fw	4876.00
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
a (Å)	14.844(1)
b (Å)	20.110(1)
c (Å)	32.186(1)
α (deg)	92.27(1)
β (deg)	100.94(1)
γ (deg)	108.25(1)
V (Å^3)	8908.1(8)
Z	2
D_{calc} (g/cm^3)	1.818
λ (Å)	0.710 79
temp (°C)	25
$R(F_o^2)^a$	0.0745
$R_w(F_o^2)^b$	0.2348

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Lengths for the Silver Atoms in Compound **1**

Ag1−O2	2.282(8)	Ag4−O6	2.165(7)	Ag7−O14	2.352(9)
Ag1−O10	2.324(9)	Ag4−O31	2.563(11)	Ag7−O15	2.362(9)
Ag1−O8	2.510(8)	Ag4−O1	2.586(8)	Ag7−Ag8	3.073(2)
Ag1−O4	2.596(8)	Ag4−Ag5	2.7704(14)	Ag7−Ag9	3.261(2)
Ag1−Ag3	2.9319(14)	Ag5−O5	2.258(7)	Ag8−O21	2.149(8)
Ag1−Ag2	2.980(2)	Ag5−O12	2.264(8)	Ag8−O16	2.189(8)
Ag2−O7	2.140(9)	Ag5−O13	2.308(9)	Ag8−Ag9	3.2952(14)
Ag2−O1	2.205(8)	Ag5−O9	2.601(8)	Ag9−O17	2.163(8)
Ag2−O1W	2.55(2)	Ag6−O22	2.228(8)	Ag9−O23	2.153(8)
Ag2−Ag4	3.206(2)	Ag6−O13	2.307(8)	Ag9−O34	2.553(12)
Ag3−O3	2.165(8)	Ag6−O3W	2.347(10)	Ag9−Ag10	2.804(2)
Ag3−O9	2.181(7)	Ag6−Ag8	3.0045(13)	Ag10−O18	2.239(8)
Ag3−O2W	2.576(9)	Ag6−Ag7	3.034(2)	Ag10−O24	2.278(8)
Ag4−O11	2.148(8)	Ag7−O20	2.209(8)	Ag10−O4W	2.386(9)
				Ag10−O19	2.501(8)

---

* Corresponding author. E-mail: Datwood@plains.nodak.edu.
[†] North Dakota State University.
[‡] The Chinese University of Hong Kong.

(1) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 5, p 808.

(2) Wei, P.; Wu, D.; Mak, T. C. W. *Inorg. Chim. Acta* **1996**, *249*, 169. Wei, P.; Li, Q.; Wu, B.; Mak, T. C. W. *Polyhedron* **1997**, *16*, 153.

(3) Wu, D.-D.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1995**, 139. Chen, X.-M.; Aubin, S. M. J.; Wu, Y.-L.; Yang, Y.-S.; Mak, T. C. W.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9600. Wong, W.-K.; Zhang, L.; Xue, F.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1997**, 1525. Wei, P.; Li, Q.; Leung, W.-P.; Mak, T. C. W. *Polyhedron* **1997**, *16*, 897.

S0020-1669(97)01276-7 CCC: $15.00

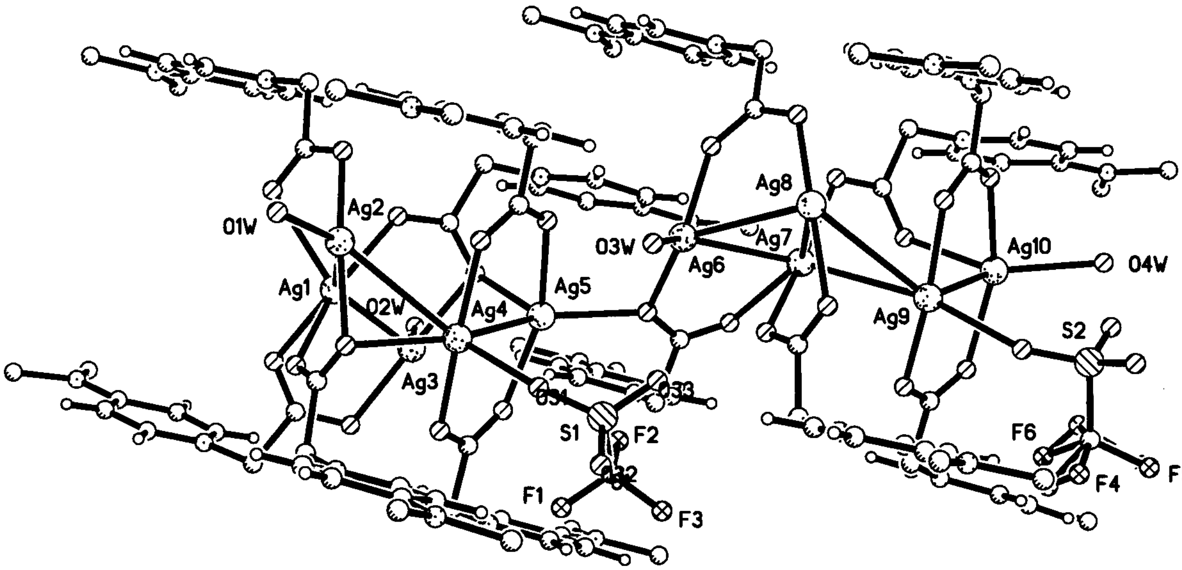

Figure 3. The octacationic cluster of compound **1**.

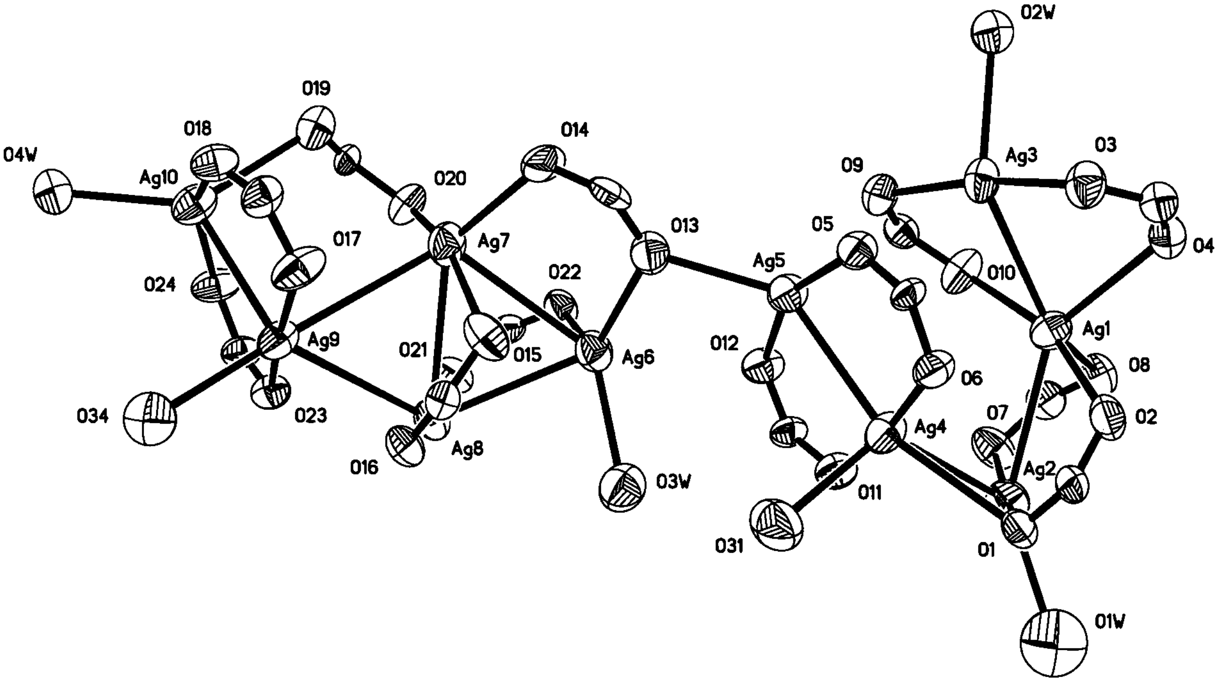

Figure 4. The carboxylate−Ag substructure in compound **1**. (Only α-carbons, oxygens, and silver atoms are shown.)

The second five-atom grouping is really just a random chain of Ag atoms. Three of them (Ag1−Ag3) are connected by close Ag−Ag bonds (~2.9−3.2 Å) and contain four bridging carboxylates (type A). This three-atom chain is linked to a two-atom unit at a longer distance (3.206(2) Å) and with a type C carboxylate. The μ_2 Ag−O distances are 2.2 and 2.6 Å.

Conclusion

An additional example of the unique bonding combinations that can be found in Ag−betaine complexes has been provided. The Ag atoms in this structure adopt geometries having coordination numbers of 4, 5, and 6. The coordination numbers do not correspond to conventional geometries such as T_d, O_h, etc. but appear to be dictated by the steric constraints of the ligands. The carboxylate ligands adopt combinations of four arrangements (Figure 2). The Ag−O bonds in type A range from 2.165(8) to 2.596(8) Å. These extremes are found for the same carboxylate bridging Ag1 and Ag3. There is one type B carboxylate forming Ag−O bonds are 2.209(8) Å to Ag7 and 2.501(8) Å to Ag10. There are two type C carboxylates with Ag−O distances of ~2.31−2.35 Å. The one type D carboxylate bridges Ag1, Ag2, and Ag4. All of the Ag−O distances are in the range of 2.2−2.6 Å. There appears, then, to be no distinct correlation between bonding arrangement and distance for either the Ag−Ag or Ag−O bonds.

Experimental Section

(4-(Dimethylamino)pyridinio)acetate (betaine II) was synthesized by the reaction of 4-(dimethylamino)pyridine with ethyl chloroacetate as described previously.[4] Analyses (C, H, N) were carried out on a Perkin-Elmer 2400 elemental analyzer. Infared spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Perkin-Elmer 1600 FT-IR spectrometer. The X-ray data were obtained on a Siemens SMART-

---

[4] Wei, P.; Li, Q.; Mak, T. C. W. *J. Chem. Crystallogr.* **1996**, *26*, 133.

CCD diffractometer with monochromated Mo radiation (Table 1). The structure (based on 12 750 data ($I > 2\sigma(I)$) was solved using the Siemens suite of programs SHELXTL-Plus.

[$Ag_{10}(L)_{12}(CF_3SO_3)_2(H_2O)_4$][$(CF_3SO_3)$]$_8$·$4H_2O$. A solution of $Ag(CF_3SO_3)$ (0.102 g, 0.40 mmol) dissolved in distilled water (5 mL) was added to a solution of L (0.144 g, 0.80 mmol) in distilled water (5 mL) at ca. 60 °C with stirring. After the resulting clear solution was cooled to room temperature and allowed to stand at room temperature for several days, colorless crystals were formed (1.3 g, 69% based on Ag). Anal. Calcd for $C_{118}H_{160}N_{24}O_{62}F_{30}S_{10}Ag_{10}$: C, 29.07; H, 3.28; N, 6.89. Found: C, 28.85; H, 3.40; N, 6.75. IR (KBr): 3417 m, 2953 w, 1652 s, 1621 s, 1606 m, 1568 s, 1514 w, 1462 w, 1387 s, 1298 m, 1266 s, 1209 m, 1159 s, 1046 m, 1032 s, 984 w, 917 w, 829 m, 749 m, 686 w, 639 m, 578 w, 518 w cm^{-1}.

Acknowledgment. This work was supported by the National Science Foundation (Grant 9452892) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 31901-AC3). The receipt of a National Science Foundation CAREER Award (Grant 9625376) is also gratefully acknowledged. T.C.W.M. thanks the Hong Kong Research Grants Council for support (Grant CUHK 4179/97P).

Supporting Information Available: A structure determination summary, tables of heavy-atom coordinates, bond lengths and angles, anisotropic parameters, and hydrogen atom coordinates, and a view of the unit cell for compound **1** (34 pages). Ordering information is given on any current masthead page.

IC971276J