Metal–Betaine Interactions. Part 3.† Crystal Structures of Polymeric Diaquabis(betaine)disilver(I) Dinitrate and Bis(pyridine betaine)disilver(I) Diperchlorate‡

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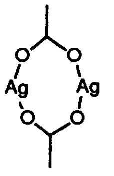
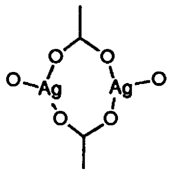
Two polymeric silver(I) complexes of betaine ($Me_3\overset{+}{N}CH_2CO_2^-$, L^1) and pyridine betaine ($C_5H_5\overset{+}{N}CH_2CO_2^-$, L^2) have been prepared and characterized by X-ray crystallography. The complexes $[\{Ag_2L^1_2(H_2O)_2(NO_3)_2\}_n]$ **1** and $[\{Ag_2L^2_2(ClO_4)_2\}_n]$ **2** are structurally similar, being composed of centrosymmetric carboxylato-bridged Ag_2(carboxylato-*O,O′*)$_2$ dimers (Ag–O 2.21–2.41 Å) which are extended into a 'stairs-like' polymer through the co-ordination of each metal centre by a carboxylate oxygen atom [Ag–O 2.47–2.50 Å] from an adjacent dimer. In addition, the primary co-ordinating sphere about the silver atom is completed by an aqua ligand [Ag–O 2.554(3) Å] in complex **1** and by a perchlorate oxygen atom [Ag–O 2.415(3) Å] in **2**. The intra-dimer Ag ··· Ag distance is 2.898(1) for **1** and 2.814(2) Å for **2**, the latter being one of the shortest among known dinuclear silver(I) carboxylates.

The poor solubility and light-sensitive nature of silver(I) carboxylates contrive to make their structural characterization difficult.[1] The reported crystal structures of silver(I) carboxylates show several different co-ordination modes, and most of them are constructed from either dimeric units or polymeric networks of dimeric sub-units. These crystal structures have been classified into four types[2] (**A**–**D**) depending on the co-ordination motif, and a number of known examples are listed in Table 1.



A



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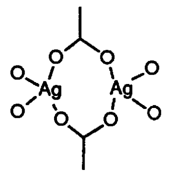

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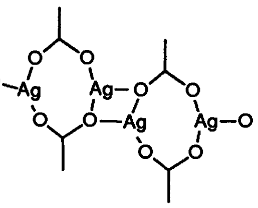
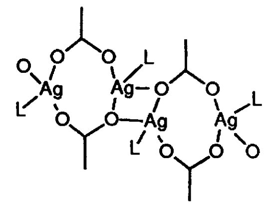


D



Modified D

As zwitterionic ligands, betaine compounds do not readily precipitate heavy-metal ions, thus providing an attractive synthetic route to the preparation of this type of carboxylate-like complex. In previous studies we have determined the crystal structures of three cadmium–betaine complexes, namely $[\{CdL^1(\mu\text{-}Cl)_2\}_n]$,[10] $[\{CdL^1(H_2O)Cl(\mu\text{-}Cl)\}_2]$[10] and $[Cd_3(L^2)_4Cl_6]$[11] (where L^1 = betaine, $Me_3\overset{+}{N}CH_2CO_2^-$; L^2 = pyridine betaine, $C_5H_5\overset{+}{N}CH_2CO_2^-$).§ In the present work, we report the preparation and characterization of two new silver(I) complexes with betaine ligands, namely diaquabis(betaine)disilver(I) dinitrate $[\{Ag_2L^1_2(H_2O)_2(NO_3)_2\}_n]$ **1** and bis(pyridine betaine)disilver(I) diperchlorate, $[\{Ag_2L^2_2(ClO_4)_2\}_n]$ **2**. Single-crystal X-ray analysis has revealed that both complexes are 'stairs-like' polymers based on centrosymmetric, carboxylate-bridged Ag_2(carboxylato-*O,O′*)$_2$ dimers.

Experimental

Complex **1** was prepared by dissolving $AgNO_3$ (0.255 g, 1.5 mmol) and betaine monohydrate (0.411 g, 3.0 mmol; Sigma) in hot water (3 cm^3, 60 °C). After cooling to room temperature, colourless prismatic crystals were afforded by very slow addition of ethanol. These are unstable in air and for X-ray work a selected crystal was sealed in a Lindemann glass capillary containing a small drop of mother-liquor. Complex **2** was prepared by mixing $AgClO_4$ (0.311 g, 1.5 mmol) and pyridine betaine[12] (0.444 g, 3.0 mmol) in hot water (3 cm^3, 60 °C). Evaporation of the solution at room temperature over 1 d yielded colourless needle crystals, which are stable in the dark.

Infrared spectra (KBr pellets) were recorded in the range 4000–400 cm^{-1} using a Nicolet 20SXC FT-IR spectrometer. Complex **1** exhibits carboxylate infrared absorption bands: ν at 1620vs, 1399vs and δ at 602m cm^{-1}. Complex **2** showed corresponding absorptions ν at 1622vs, 1606vs, 1382s and δ at 705m cm^{-1}. The carboxylate group absorptions in complex **1** are distinguishable from those of the uncomplexed betaine (ν at 1624 and 1388 cm^{-1}).[13] The separation (Δ) between $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ for **1** is 221 cm^{-1}, which is smaller than that in uncomplexed betaine (236 cm^{-1}) and hence indicative of the chelating and bridging mode adopted.[14] A similar smaller Δ value has also been observed for $[(CdL^1Cl_2)_n]$ (Δ = 224 cm^{-1}), in which the carboxylate group of L^1 acts as a bridging ligand.[10] Likewise the Δ value (av. 232 cm^{-1}) in complex **2** is also significantly smaller than that (Δ = 254 cm^{-1}) found in uncomplexed pyridine betaine (ν = 1631 and 1377 cm^{-1})[12] and matches those observed for $[\{MnL^2_2(H_2O)_2Cl_2\}_n]$ (Δ = 234

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† Part 2 is ref. 10.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

§ The IUPAC names of these two compounds are trimethylammonioacetate and pyridinioacetate respectively.

Table 1 Typical silver(I) carboxylates having different types of dimeric structures

Type	Examples	Ag • • • Ag/Å	Ref.
A	$[Ag_2(o\text{-}HOC_6H_4CO_2)_2]$	2.861(1)	3
	$[Ag_2(PhCO_2)_2]$	2.92(1)	4
	$[Ag_2(p\text{-}HOC_6H_4CO_2)_2]\cdot H_2O$	2.90(1)	4
B	$[Ag_2(o\text{-}NH_2COC_6H_4OCH_2CO_2)_2]$	3.001(1)	2
	$[Ag_2\{NH_3(CH_2)_2CO_2\}_2(NO_3)_2]$	2.855(4)	5
C	$[Ag_2\{CF_3(CF_2)_2CO_2\}_2]$	2.90(2)	6
D	$[\{Ag_2(F_3CCO_2)_2\}_n]$	2.967(3)	7
	$[\{Ag_2(NH_3CH_2CO_2)_2(NO_3)_2\}_n]$	2.877(6)	8
Modified **D**	$[\{Ag_2(C_6H_5CO_2)_2(C_5H_5N)_2\}_n]$	2.956(2), 2.902(2)	9
	1 $[\{Ag_2L^1{}_2(H_2O)_2(NO_3)_2\}_n]$	2.898(1)	This work
	2 $[\{Ag_2L^2{}_2(ClO_4)_2\}_n]$	2.814(2)	This work

Table 2 Data collection and processing parameters[a]

Complex	1	2
Formula	$C_{10}H_{26}Ag_2N_4O_{12}$	$C_{14}H_{14}Ag_2Cl_2N_2O_2$
M	610.09	688.91
Colour and habit	Colourless prism	Colourless needle
a/Å	5.6589(3)	5.3657(7)
b/Å	15.813(2)	15.133(3)
c/Å	11.549(2)	13.041(4)
β/°	98.10(1)	99.54(2)
U/Å^3	1023.1(2)	1044.2(4)
Z	2	2
D_m/g cm^{-3}	1.972	2.171
D_c/g cm^{-3}	1.980	2.181
μ/mm^{-1}	1.96	2.18
Crystal size/mm	0.12 × 0.20 × 0.30	0.08 × 0.14 × 0.30
Mean μr	0.203	0.187
Collection range	$h, k, \pm l$; $2\theta_{max} = 55°$	$h, k, \pm l$; $2\theta_{max} = 55°$
Unique data measured	1808	1851
Obs. data with $I \geqslant 3\sigma(I)$, n	1483	1358
No. of variables, p	128	145
R[b]	0.028	0.056
R'[c]	0.035	0.068
S[d]	1.512	1.558
Residual extrema in final difference map e Å^{-3}	+0.46, −0.37	+1.43, −1.21

[a] Details in common: space group $P2_1/c$, Mo-Kα radiation (λ = 0.710 73 Å). [b] $R = \Sigma\|F_0| - |F_c\|/\Sigma|F_0|$. [c] $R' = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{\frac{1}{2}}$ where $w = [\sigma^2(F_0) + 0.002|F_0|^2]^{-1}$ for **1** and $[\sigma^2(F_0) + 0.001|F_0|^2]^{-1}$ for **2**. [d] $S = [\Sigma w(|F_0| - |F_c|)^2/(n - p)]^{\frac{1}{2}}$.

Table 3 Atomic coordinates (× 10^4) for complexes **1** and **2**

Atom	x	y	z
$[\{Ag_2L^1{}_2(H_2O)_2(NO_3)_2\}_n]$ **1**			
Ag(1)	2147(1)	498(1)	4997(1)
O(1w)	1808(6)	299(2)	2784(3)
O(1)	−202(5)	1560(2)	5429(3)
O(2)	−3613(5)	883(2)	4877(2)
C(1)	−2411(6)	1487(2)	5299(3)
C(2)	−3917(6)	2207(2)	5672(3)
N(1)	−2659(5)	2974(2)	6254(3)
C(3)	−1239(8)	3428(2)	5442(4)
C(4)	−4561(8)	3566(3)	6572(4)
C(5)	−1058(8)	2735(3)	7353(3)
N(2)	−3180(6)	−1013(2)	1905(3)
O(3)	−3684(9)	−537(2)	2665(3)
O(4)	−1605(9)	−798(3)	1353(4)
O(5)	−4110(8)	−1691(2)	1731(3)
$[\{Ag_2L^2{}_2(ClO_4)_2\}_n]$ **2**			
Ag(1)	2306(1)	377(1)	469(1)
Cl(1)	3124(5)	1082(2)	3112(2)
O(3)	3807(22)	573(8)	2305(7)
O(4)	4160(19)	1929(6)	3029(10)
O(5)	4204(19)	678(6)	4070(6)
O(6)	500(15)	1169(6)	3023(8)
O(1)	−19(11)	1589(4)	367(5)
O(2)	−3740(12)	924(4)	−36(6)
C(1)	−2318(16)	1561(5)	304(6)
C(2)	−3722(18)	2381(6)	571(8)
N(1)	−1934(13)	3030(4)	1120(5)
C(3)	−609(20)	3558(6)	584(8)
C(4)	1186(20)	4113(6)	1087(9)
C(5)	1608(22)	4136(7)	2152(10)
C(6)	281(24)	3597(7)	2683(8)
C(7)	−1535(20)	3048(7)	2164(7)

cm^{-1})[12] and $[Cd_3L^2{}_4Cl_6]$ (Δ = 238 cm^{-1}),[11] where the carboxylate group of L^2 adopts a bridging mode.

For each complex, determination of the crystal class, orientation matrices and cell dimensions on a Nicolet R3m/V diffractometer were performed according to established procedures.[15] Diffraction intensities were collected at 21 °C, and the parameters are summarized in Table 2. The raw data were processed with the learnt-profile procedure,[16] and absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of selected reflections over a range of 2θ angles.[17]

Both crystal structures were solved with the Patterson superposition method. The hydrogen atoms of organic ligands were generated geometrically (C–H bonds fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their respective parent C atoms; the H atoms of the aqua ligand in complex **1** were located in a difference map and included in structure-factor calculations in the last stage of full-matrix least-squares refinement.

All computations were performed on a DEC MicroVAX-II computer with the SHELXTL-PLUS program package.[18,19] Analytic expressions of neutral-atom scattering factors were employed.[20] The final discrepancy indices and other parameters at the conclusion of refinement are given in Table 2, atomic positional parameters in Table 3 and selected interatomic distances and bond angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

$[\{Ag_2L^1{}_2(H_2O)_2(NO_3)_2\}_n]$ **1**.—Complex **1** is a polymer based on bis(carboxylato-*O*,*O*′)-bridged centrosymmetric Ag$_2$-L$^1{}_2$ dimers (Fig. 1), with an Ag . . . Ag separation [2.898(1) Å] essentially equal to that [2.89 Å] found in metallic silver, thus indicating a comparable extent of metal–metal interaction. The intra-dimer Ag–O distances and O–Ag–O angle are 2.241(3), 2.334(3) Å and 154.7(1)°, respectively, which are comparable to those found in the dimeric structures of several known silver(I) carboxylates (Table 1). The present structure is extended into a stairs-like polymer running parallel to the *a* axis *via* metal–carboxylate linkages [Ag(1)–O(2e) 2.497(3) Å] between adjacent dimers, generating centrosymmetric rhombic Ag$_2$O$_2$ units as found in a type **D** structure.[1] Furthermore, each Ag^I

Table 4 Selected interatomic distances (Å) and angles (°) for complexes **1** and **2**

$[\{Ag_2L^1{}_2(H_2O)_2(NO_3)_2\}_n]$ **1**			
Ag(1)–Ag(1a)	2.898(1)	Ag(1)–O(1w)	2.554(3)
Ag(1)–O(1)	2.241(3)	Ag(1)–O(2e)	2.497(3)
Ag(1)–O(2a)	2.334(3)		
O(1)–C(1)	1.243(5)	O(2)–C(1)	1.233(4)
C(1)–C(2)	1.521(5)	C(2)–N(1)	1.514(4)
O(1w)–Ag(1)–O(1)	110.6(1)	O(1w)–Ag(1)–Ag(1a)	89.5(1)
O(1)–Ag(1)–Ag(1a)	83.3(1)	O(1w)–Ag(1)–O(2e)	85.0(1)
O(1)–Ag(1)–O(2e)	115.8(1)	Ag(1a)–Ag(1)–O(2e)	160.9(1)
O(1w)–Ag(1)–O(2a)	85.6(1)	O(1)–Ag(1)–O(2a)	154.7(1)
Ag(1a)–Ag(1)–O(2a)	77.4(1)	O(2e)–Ag(1)–O(2a)	84.0(1)
Ag(1)–O(1)–C(1)	121.5(2)	C(1)–O(2)–Ag(1b)	130.4(3)
C(1)–O(2)–Ag(1a)	121.9(2)	Ag(1b)–O(2)–Ag(1a)	96.0(1)
O(1)–C(1)–O(2)	127.5(4)	O(1)–C(1)–C(2)	119.4(3)
O(2)–C(1)–C(2)	113.1(3)	C(1)–C(2)–N(1)	118.6(3)
Hydrogen bonding			
O(1w) ··· O(3e)	2.894(7)	O(1w) ··· O(4)	2.928(6)
O(3e) ··· O(1w) ··· O(4)	102.6(3)		
$[\{Ag_2L^2{}_2(ClO_4)_2\}_n]$ **2**			
Ag(1)–Ag(1a)	2.814(2)	Ag(1)–O(3)	2.415(9)
Ag(1)–O(1)	2.211(6)	Ag(1)–O(2e)	2.466(7)
Ag(1)–O(2a)	2.220(6)		
O(1)–C(1)	1.22(1)	O(2)–C(1)	1.26(1)
C(1)–C(2)	1.52(1)	C(2)–N(1)	1.47(1)
O(3)–Ag(1)–O(1)	92.9(3)	O(3)–Ag(1)–Ag(1a)	127.3(3)
O(1)–Ag(1)–Ag(1a)	82.1(1)	O(3)–Ag(1)–O(2e)	93.6(3)
O(1)–Ag(1)–O(2e)	102.0(2)	Ag(1a)–Ag(1)–O(2e)	138.9(2)
O(3)–Ag(1)–O(2a)	106.8(3)	O(1)–Ag(1)–O(2a)	159.5(2)
Ag(1a)–Ag(1)–O(2a)	81.2(2)	Ag(1)–O(3)–Cl(1)	136.6(7)
Ag(1)–O(1)–C(1)	121.8(5)	C(1)–O(2)–Ag(1a)	131.2(6)
Ag(1a)–O(2)–Ag(1b)	96.9(2)	O(2e)–Ag(1)–O(2a)	83.1(2)
O(1)–C(1)–O(2)	126.5(8)	O(1)–C(1)–C(2)	119.2(7)
O(2)–C(1)–C(2)	114.2(8)	C(1)–C(2)–N(1)	110.4(7)

Symmetry codes: for **1**: a $-x, -y, 1-z$; b $-1+x, y, z$; c $-1-x, -y, 1-z$; d $1-x, -y, 1-z$; e $1+x, y, z$; for **2** a $-x, -y, -z$; b $-1+x, y, z$; c $-1-x, -y, -z$; d $1-x, -y, -z$; e $1+x, y, z$.

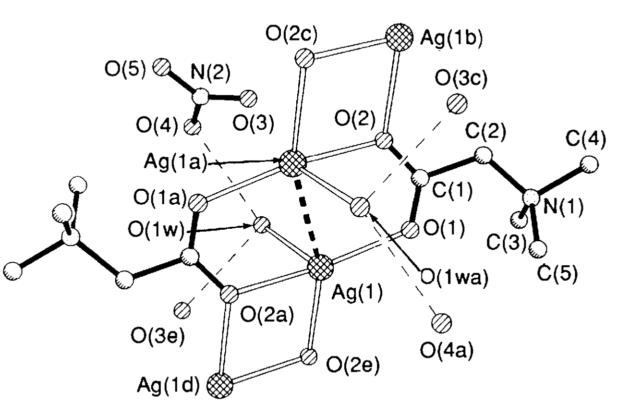

Fig. 1 Perspective view showing the dimeric structure of $[\{Ag_2L^1{}_2(H_2O)_2(NO_3)_2\}_n]$ **1** and the atom-numbering scheme. Hydrogen bonds are represented by fine broken lines. Symmetry codes are given in Table 4

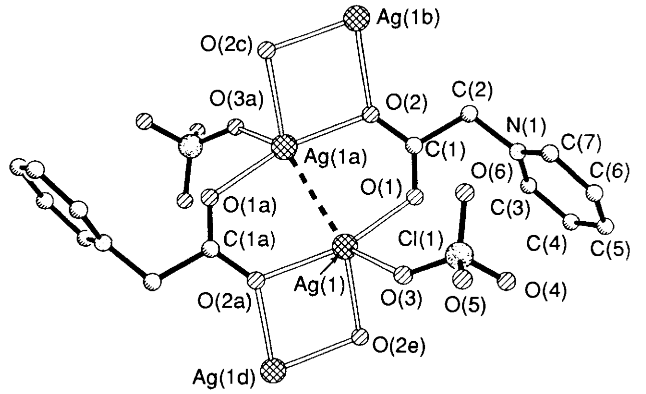

Fig. 2 Perspective view showing the dimeric structure of $[\{Ag_2L^2{}_2(ClO_4)_2\}_n]$ **2** and the atom-numbering scheme. Symmetry codes are given in Table 4

atom is also co-ordinated by an aqua ligand in an axial site [Ag–O(1w) 2.554(3) Å], giving complex **1** a modified type **D** structure similar to that found in bis(μ-benzoato)bis(pyridine)disilver(I),[9] in which the axial site is occupied by a pyridine nitrogen atom. Each nitrate group [N–O 1.21(1) Å, O–N–O 120(2)°] forms two hydrogen bonds with neighbouring aqua ligands [O(1w) ··· O(3e) 2.832(7), O(1w) ··· O(4) 2.981(6) Å, O(3e) ··· O(1w) ··· O(4) 102.6(4)°]. By contrast, nitrate groups are commonly found bound directly to silver in silver nitrate complexes containing other ligands. The dimeric structure found in complex **1** is also different from those found in silver(I) complexes of analogous ligands such as the zwitterionic amino acids, *e.g.* alaninesilver(I) nitrate[5] or glycine silver(I) nitrate,[8] which have type **B** and **D** dimeric structures, respectively.

$[\{Ag_2L^2{}_2(ClO_4)_2\}_n]$ **2**.—The structure of complex **2** is similar to that of **1**, being also a modified type **D** stairs-like polymer based on bis(carboxylato-*O,O'*)-bridged, centrosymmetric dimers (Fig. 2); the one-dimensional polymeric chains run parallel to the *a* axis in the unit cell. The intra-dimer Ag ··· Ag distance [2.814(2) Å], although slightly longer than that (2.78 Å) found in the unusual dinuclear silver(I) carboxylate complex, bis(3-hydroxy-2,2,3-trimethyl-4-phenylcyclohexanecarboxylato)disilver(I) dihydrate,[21] is considerably shorter (by more than 0.04 Å) than those in other known dinuclear silver(I) carboxylates (Table 1) and in metallic silver, thus indicating a significantly stronger metal–metal interaction. The intra-dimer Ag–O distances and O–Ag–O angle are 2.211(6), 2.220(6) Å and 159.5(2)°, respectively; these bond lengths are significantly shorter and the angle significantly larger than those for complex **1**. The axial Ag–O bond distances are 2.446(7) and 2.415(9) Å for silver–adjacent carboxylate and silver–perchlorate interactions, respectively. Both axial Ag–O bonds are significantly shorter than those in **1**. Hitherto only one example of a carboxylato complex containing an axially bound perchlorate ligand has been found *viz.*, di-μ-[(2-chlorophenoxy)ethanoato]-disilver(I)]-silver(I) perchlorate, **3**,[22] which has the type **B** structure. Thus the axially bound perchlorate group [Cl–O 1.41(1) Å, O–Cl–O 109.5(28)°] in complex **2** distinguishes it from complexes **1** and **3** and constitutes a new structural variety among silver(I) carboxylates.

Finally, it is worth noting that the present complexes are nearly isostructural, with the nitrate group *and* aqua ligand playing the same role in **1** as the perchlorate group in **2**.

Acknowledgements

This work was supported in part by an Earmarked Grant for Research from the University and Polytechnic Grants Committee, Hong Kong.

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Received 30*th August* 1990; *Paper* 0/03918G