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Monomeric and polymeric structures of silver salts of cobalt(III) bis(dicarbollide) ions

Chi-Wing Tsang [a], Jie Sun [b], Zuowei Xie [a,*]

[a] *Department of Chemistry, The Chinese University of Hong Kong, Shatin NT, Hong Kong, People's Republic of China*
[b] *Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China*

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Abstract

The coordination chemistry of cobalt(III) bis(dicarbollide) ions is explored by studying the crystal structures of their silver(I) salts. Each structure has a different coordination motif, which could not be predicted from knowledge of the constituent parts, showing the subtlety and diversity of silver–carborane coordination chemistry. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Carborane; Cobalt bis(dicarbollide); Silver; Structure

1. Introduction

Icosahedral carboranes constitute a class of robust and weakly coordinating anions and have recently received much attention [1]. They play a very important role in stabilizing coordinatively unsaturated cations such as the silylium ion (R_3Si^+) [2–4], the four-coordinate tetraphenylporphyrinatoiron(III) ion ($(Fe(tpp)^+)$) [5], carbocations [6,7], and in enhancing the reactivity of organolanthanide cations [8]. Silver(I) salts of carborane anions are very useful halide metathesis reagents for introducing weakly coordinating anions into complexes and they are finding immediate applications in metathesis, catalysis and oxidation chemistry [9–12]. They have also been shown to possess a rich structural and coordination chemistry of their own. In all known crystallographically characterized silver(I) carborane complexes [5,9b,13–17] each structure has a different coordination motif which could not be predicted from a knowledge of the constituent parts. Some patterns are beginning to emerge. All these works have, however, focused on $CB_{11}H_{12}^-$, $CB_9H_{10}^-$ and their derivatives. The coordination chemistry of the cobalt bis(dicarbollide) ion and its derivatives has remained largely unexplored although these anions have been shown to be very useful counterions in making cationic organometallic compounds [11,18] and efficient extractants of ^{137}Cs, ^{90}Sr and ^{152}Eu from nuclear wastes [19]. Since cobalt bis(dicarbollide) ions contain two icosahedral cages, it is anticipated that these ions might have the richer coordination chemistry than CB_{11} and CB_9 systems. We would like to explore this chemistry by studying the crystal structures of the silver(I) salts of three cobalt(III) bis(dicarbollide) ions, (η^2-*p*-xylene)Ag[$Co(C_2B_9H_{11})_2$] (**1**), (η^2-*p*-xylene)Ag[8,8′-μ-1,2-C_6H_4–$Co(C_2B_9H_{10})_2$]1.5(*p*-xylene) (**2**) and [$(CH_3CN)_4Ag$][$Co(C_2B_9H_8Br_3)_2$] (**3**).

2. Results and discussion

2.1. Preparation

Both Ag[$Co(C_2B_9H_{11})_2$] and Ag[8,8′-μ-1,2-C_6H_4–$Co(C_2B_9H_{10})_2$] have good solubility in arene solvents and X-ray-quality crystals were obtained by slow evaporation of a *p*-xylene solution at r.t. In contrast, Ag[$Co(C_2B_9H_8Br_3)_2$] is almost insoluble in pure arene solvents and had to be recrystallized from solvent mixtures such as CH_3CN–*p*-xylene. As a result, complex **3** was isolated. It is noted that no CH_3CN coordinated silver(I) complexes were obtained if silver(I) salt of

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* Corresponding author. Tel.: +852-26096269; fax: +852-26035057.
E-mail address: zxie@cuhk.edu.hk (Z. Xie).

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polybromo- or polyiodo-carboranes of CB_{11} or CB_9 systems were recrystallized from a CH_3CN–arene solution [14,16].

2.2. Crystal structures

An X-ray analysis reveals that in (η^2-*p*-xylene)$Ag[Co(C_2B_9H_{11})_2]$ (**1**), the silver atom is bound to one *p*-xylene molecule in an η^2-fashion and three B–H bonds from the three dicarbollide cages through H(8), H(8′) and H(9A) atoms in a distorted-tetrahedral geometry, shown in Fig. 1. The tridentate $Co(C_2B_9H_{11})_2^-$ and Ag^+ ions serve as alternating bridging ligands to give a zigzag cation–anion chain that is maintained in one-dimension throughout the lattice. The asymmetric η^2-fashion of *p*-xylene bonding, with Ag–C bond distances of 2.562(7) and 2.411(7) Å, is typical of many silver–arene complexes [20]. The Ag–B(8) distance of 2.705(6) Å is slightly longer than those (2.50–2.68 Å) normally observed in silver-carborane complexes [13,14b,16,17]. The Ag–B(8′) and Ag–B(9A) distances (2.926(6) and 2.938(6) Å) are significantly longer than the Ag–B(8) one, and they are the longest Ag–B distances reported in the literature [21]. The Ag–H distances, however, fail in a short range 2.01–2.08 Å, which are comparable to those (1.97–2.24 Å) reported in the literature for silver–carborane complexes [13,14b,16,17]. These results indicate that Ag has much stronger interactions with H atoms than B atoms in **1**. Interestingly, the location of the three coordinating B–H groups involves that portion of the carborane cage which is believed to be the most nucleophilic/electron-rich [22,23]. The Co–C, Co–B, C–C, C–B and B–B distances in **1** are all comparable to those found in $Cs[Co(C_2B_9H_{11})_2]$ [24]. It is noted that this dicarbollide complex has been observed to exist in a '*cisoid*' structure in which the polyhedral carbon atoms of the opposing ligand cages reside on the same side of the molecule in a staggered configuration. This phenomenon may be caused by the Ag···H(8′)–B(8′) and Ag···H(8)–B(8) interactions which force the carbon atoms of the icosahedral cages to be on the same side of the molecule.

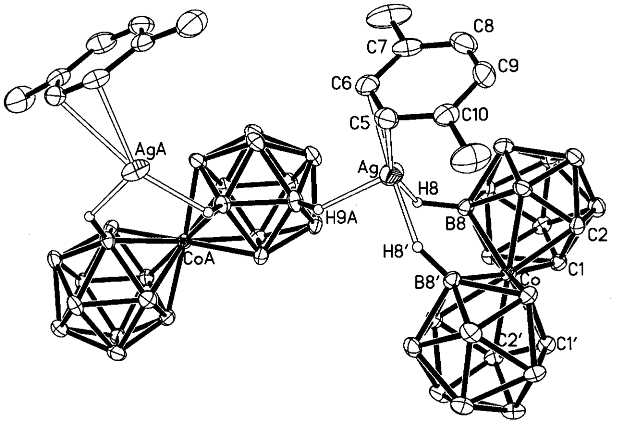

Fig. 1. Perspective view of the coordinating sphere around the silver atom in **1**.

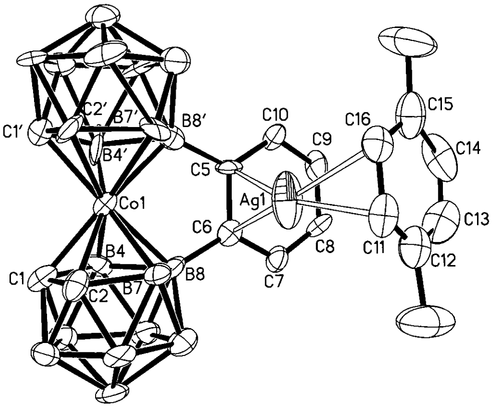

Fig. 2. Perspective view of **2** showing one of the two crystallographically independent molecules (solvate *p*-xylene molecules are not shown).

If the two coordinating sites, B(8) and B(8′), in complex **1** are linked by an aromatic ring, what's the coordination chemistry of the resulting anion? Fig. 2 shows the molecular structure of (η^2-*p*-xylene)Ag[8,8′-μ-1,2-C_6H_4–$Co(C_2B_9H_{10})_2$]. Its coordination motif differs significantly from that of **1**. It is interesting to note that no interaction between the Ag^+ and any B–H bonds from the cage is observed. The Ag atom is η^2-bound to each of two aromatic rings in an approximately linear geometry. The average distances from the Ag atom to two aromatic rings are about the same (2.45(2) versus 2.42(2) Å), perhaps indicating that the π-donor ability of the *p*-xylene molecule is no different than that of the bridging aromatic ring in complex **2**. The two aromatic rings are not parallel to each other and they are separated by about 4.1 Å. There are two crystallographically independent molecules in the unit cell, which are associated to each other through a π–π interaction between the bridging aromatic ring and the *p*-xylene of the second molecule of **2** (Fig. 3). These two aromatic rings are laterally shifted and the shortest contact is 3.32 Å from C34 to the mean plane of the bridging aromatic ring. Such a weak intermolecular π–π interaction is maintained in one dimension throughout the lattice, resulting in the formation of a π–π polymer.

Bromination of the cobalt(III) bis(dicarbollide) ion gave the hexabrominated derivative $Co(8,9,12\text{-}Br_3\text{–}C_2B_9H_8)_2^-$. Its silver(I) salt has been subjected to an X-ray analysis. Fig. 4 shows the molecular structure of **3**. Unlike complexes **1** and **2**, it is an ionic complex composed of discrete ions $Ag(CH_3CN)_4^+$ and $Co(C_2B_9H_8Br_3)_2^-$. The crystal packing is shown in Fig. 5. The Ag atom sits on a two-fold axis, and the Co

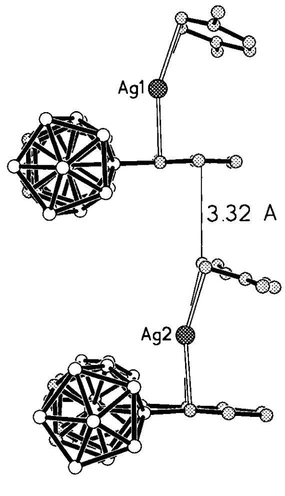

Fig. 3. Intermolecular π–π interaction in **2**.

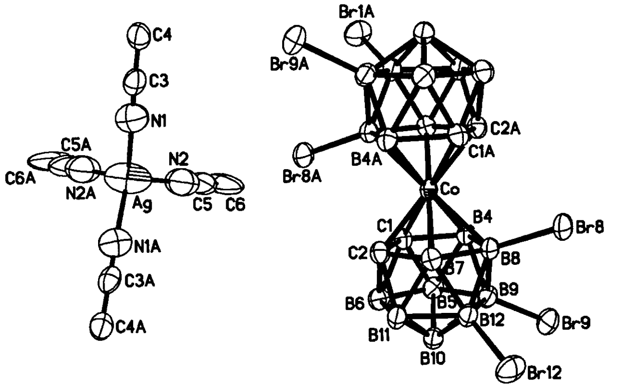

Fig. 4. Perspective view of **3**.

atom sits at an inversion center. The four-coordinate geometry about silver is very similar to that found in $[Ag(CH_3CN)_4]ClO_4$ [25]. It is noteworthy that the Ag atom does not have any interactions with any bromine atoms on the carborane cage, which has not been observed before in silver salts of halocarboranes. The average Ag–N distance of 2.25(3) Å and the average N–Ag–N angle of 109.5(10)° are close to the corresponding values of 2.26(3) Å and 109.4(10)° found in $[Ag(CH_3CN)_4]ClO_4$, respectively. The bond distances and angles observed in $Co(C_2B_9H_8Br_3)_2^-$ are very similar to those found in the anion of $[Me_4N][Co(C_2B_9H_8Br_3)_2]$ [23].

In summary, the first crystallographically characterized examples of silver salts of cobalt(III) bis(dicarbollide) ions have been reported. Each structure has a different coordination motif which could not been predicted from a knowledge of the constituent parts, demonstrating a diverse and rich coordination chemistry of the cobalt(III) bis(dicarbollide) ions. The bridging anion motif is very common to all known silver–carboranes of CB_{11} and CB_9 systems, but is not common to silver–cobaltabis(dicarbollide) derivatives. As evidenced by this work, both monomeric and polymeric structures of the silver salts of carborane ions have been observed, and the molecules could be linked to each other via Ag···H–B or π–π interactions.

3. Experimental

3.1. Preparation of silver(I) salts

Complexes $Ag[Co(C_2B_9H_{11})_2]$ [9a], $Ag[Co(C_2B_9H_8Br_3)_2]$ [9a] and $Cs[8,8'\text{-}\mu\text{-}1,2\text{-}C_6H_4\text{–}Co(C_2B_9H_{10})_2]$ [26] were prepared according to the literature methods. $Ag[8,8'\text{-}\mu\text{-}1,2\text{-}C_6H_4\text{–}Co(C_2B_9H_{10})_2]$ was readily achieved by treatment of $Cs[8,8'\text{-}\mu\text{-}1,2\text{-}C_6H_4\text{–}Co(C_2B_9H_{10})_2]$ with 1.1 equivalents of $AgNO_3$ in H_2O at r.t. according to the literature procedures [9a]. Since these complexes are light sensitive, it is better to have the reaction vessels covered with the aluminum foil. X-ray quality crystals of **1** and **2** were grown by slow evaporation of a *p*-xylene solution of $Ag[Co(C_2B_9H_{11})_2]$ and $Ag[8,8'\text{-}\mu\text{-}1,2\text{-}C_6H_4\text{–}Co(C_2B_9H_{10})_2]$ at r.t., respectively. Single crystals of **3** were obtained via slow evaporation of a CH_3CN–*p*-xylene solution of $Ag[Co(C_2B_9H_8Br_3)_2]$ at r.t. A donor solvent such as CH_3CN must be used since **3** is almost insoluble in pure arenes.

3.2. X-ray structure determination

All single crystals were immersed in Paratone-N oil and sealed in thin-walled glass capillaries. Data were collected on a Rigaku AFC7R diffractometer using Mo–K_α radiation from a Rigaku rotating-anode X-ray generator operating at 40 kV and 100 mA. An absorption correction was applied by correlation of symmetry-equivalent reflections using the ABSCOR program [27], or using an empirical ψ-scan method. All structures were solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the Siemens SHELXTL-V 5.03 program package (PC version) [28]. Most of the carborane hydrogen atoms were located from difference Fourier syntheses. All other hydrogen atoms were geometrically fixed using the riding model. For noncentrosymmetric structures, the appropriate enantiomorph was chosen by refining Flack's parameter x toward 0 [29]. The cage carbon atoms in complex **1** were identified by the two criteria of interatomic distances and temperature factors. Table 1 gives crystal data and details of data collection and structure refinement. Selected bond distances are listed in Table 2. Further details are included in the supplementary material.

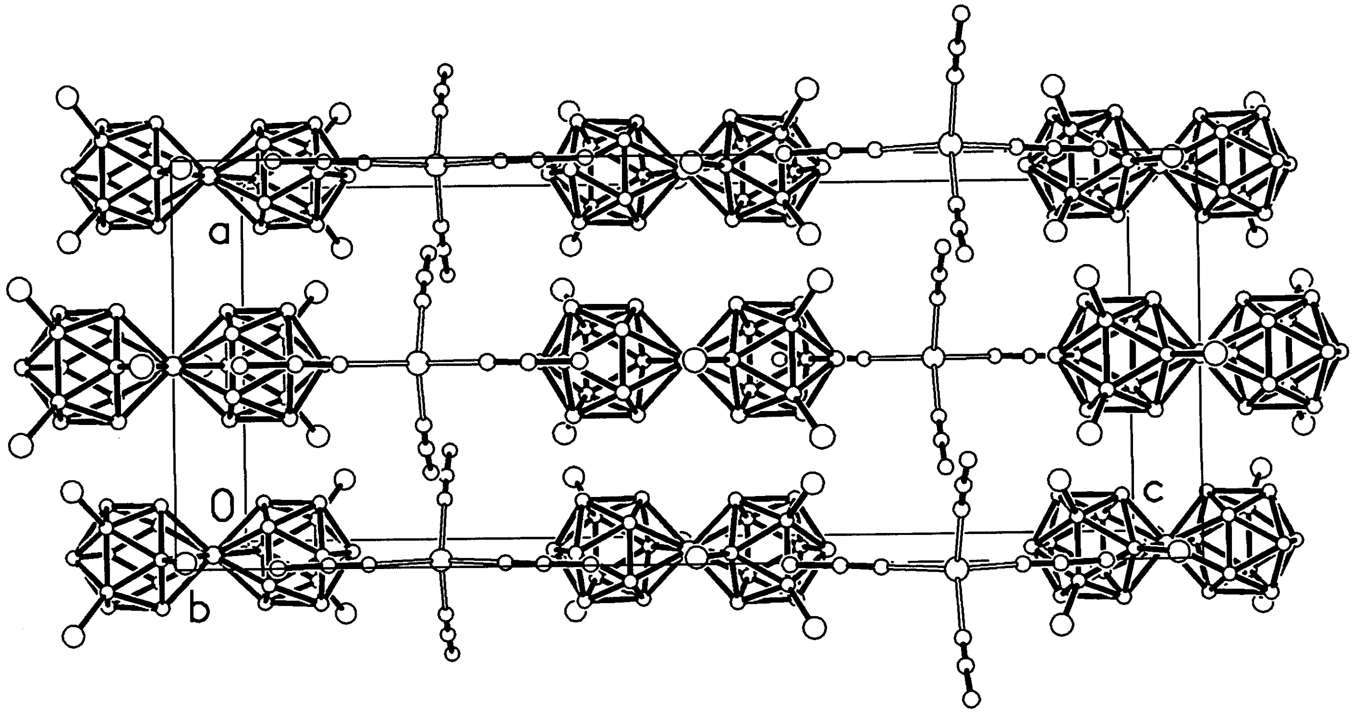

Fig. 5. Crystal packing of **3**.

Table 1
Crystal data and summary of data collection and refinement for **1**–**3**

	(η^2-*p*-Xylene) Ag[Co($C_2B_9H_{11}$)$_2$] (**1**)	(η^2-*p*-Xylene)Ag[8,8′-μ-1,2-C_6H_4Co($C_2B_9H_{10}$)$_2$]· 1.5(*p*-xylene) (**2**)	[(CH_3CN)$_4$Ag] [Co($C_2B_9H_8Br_3$)$_2$] (**3**)
Empirical formula	$C_{12}H_{32}AgB_{18}Co$	$C_{60}H_{98}Ag_2B_{36}Co_2$	$C_{12}H_{28}AgB_{18}Br_6CoN_4$
Crystal size (mm)	0.20 × 0.40 × 0.60	0.15 × 0.20 × 0.30	0.20 × 0.20 × 0.30
Formula weight	537.8	1542.1	1069.2
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*Pc*	$P2_1$	$C2/c$
Unit cell dimensions			
a (Å)	10.573(1)	14.130(3)	10.766(2)
b (Å)	12.851(1)	15.894(3)	12.656(3)
c (Å)	9.694(1)	16.974(3)	26.862(3)
β (°)	116.46(1)	90.24(3)	90.16(2)
V (Å^3)	1179.2(2)	3812(1)	3660(1)
Z	2	2	4
D_{calc} (Mg m^{-3})	1.515	1.344	1.940
Radiation (λ) (Å)	Mo–K$_\alpha$ (0.71073)	Mo–K$_\alpha$ (0.71073)	Mo–K$_\alpha$ (0.71073)
2θ Range (°)	3.0–50.0	4.5–50.0	5.0–50.0
μ (mm^{-1})	1.534	0.972	7.554
F(000)	536	1572	2008
Number of observed reflections	2085	4515	2086
Number of parameters refined	289	791	174
Goodness-of-fit	0.974	1.065	1.083
R_1	0.0265	0.0875	0.0480
wR_2	0.0719	0.2455	0.1255

Table 2
Selected bond distances (Å) [a]

Complex (η^2-p-xylene)Ag[Co($C_2B_9H_{11}$)$_2$] ***(1)***			
Ag–B(8)	2.705(6)	Co–C(1′)	2.052(5)
Ag–B(8′)	2.926(6)	Co–C(2′)	2.046(6)
Ag–B(9) # 1	2.938(6)	Co–B(4)	2.107(5)
Ag–C(5)	2.562(7)	Co–B(7)	2.091(7)
Ag–C(6)	2.411(7)	Co–B(8)	2.103(6)
C(1)–C(2)	1.610(7)	Co–B(4′)	2.107(6)
C(1′)–C(2′)	1.613(7)	Co–B(7′)	2.088(6)
Co–C(1)	2.064(5)	Co–B(8′)	2.1116(6)
Co–C(2)	2.057(5)		
Complex (η^2-p-xylene)Ag[8,8′-μ-1,2-C_6H_4Co($C_2B_9H_{10}$)$_2$] ***(2)***			
Ag(1)–C(5)	2.43(2)	Co(1)–C(1)	2.06(2)
Ag(1)–C(6)	2.48(2)	Co(1)–C(2)	2.11(2)
Ag(1)–C(11)	2.37(2)	Co(1)–C(1′)	2.08(2)
Ag(1)–C(16)	2.43(2)	Co(1)–C(2′)	2.06(2)
Ag(2)–C(23)	2.38(2)	Co(2)–C(21)	1.98(2)
Ag(2)–C(24)	2.50(2)	Co(2)–C(22)	2.15(2)
Ag(2)–C(29)	2.41(2)	Co(2)–C(21′)	2.04(2)
Ag(2)–C(34)	2.47(3)	Co(2)–C(22′)	2.02(2)
Co(1)–B(4)	2.05(2)	Co(1)–B(4′)	1.91(5)
Co(1)–B(7)	2.10(2)	Co(1)–B(7′)	2.15(2)
Co(1)–B(8)	2.12(2)	Co(1)–B(8′)	2.12(2)
Co(2)–B(24)	2.05(2)	Co(2)–B(24′)	2.10(3)
Co(2)–B(27)	2.10(2)	Co(2)–B(27′)	2.11(2)
Co(2)–B(28)	2.12(2)	Co(2)–B(28′)	2.05(2)
Complex [(CH_3CN)$_4$Ag][Co($C_2B_9H_8Br_3$)$_2$] ***(3)***			
Ag–N(1)	2.31(2)	Co–B(4)	2.11(1)
Ag–N(2)	2.19(3)	Co–B(7)	2.09(1)
Ag–N(1) # 2	2.31(2)	Co–B(8)	2.15(2)
Ag–N(2) # 2	2.19(3)	Co–B(4) # 3	2.11(1)
Co–C(1)	2.02(1)	Co–B(7) # 3	2.09(1)
Co–C(2)	2.01(1)	Co–B(8) # 3	2.15(2)
Co–C(1) # 3	2.02(1)	Br(8)–B(8)	1.96(1)
Co–C(2) # 3	2.01(1)	Br(9)–B(9)	1.95(2)
		Br(12)–B(12)	1.96(2)

[a] Symmetry transformations used to generate equivalent atoms: (# 1) $x, y, 1/2+z$; (# 2) $-x-1, y, -z-1/2$; (# 3) $-x, -y+1, -z$.

4. Supplementary material

Crystallographic data for the structural analyses (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 143997 for compound **1**, CCDC no. 143998 for compound **2** and CCDC no. 143999 for compound **3**, respectively. Copies of the data may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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