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Coordination Polymers with Carborane Anions: Silver Dinitrile Complexes

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Crystalline materials have been isolated and characterized from mixing the silver carborane salts $Ag(CB_{11}H_{12})$ or $Ag[Co(C_2B_9H_{11})_2]$ with nitrile ligands, either terminal acetonitrile or potentially bridging alkanedinitriles. Most of the complexes showed B–H$\cdots$Ag interactions between the silver center and carborane anion. [Ag(acetonitrile)$_2$($CB_{11}H_{12}$)] has a hexagonal network structure. [Ag(malonitrile)$_2$($CB_{11}H_{12}$)] is a discrete dimeric complex, while [Ag$_4$(succinonitrile)$_5$($CB_{11}H_{12}$)$_4$], [Ag(glutaronitrile)$_2$][$Co(C_2B_9H_{12})_2$], and {Ag(glutaronitrile)[$Co(C_2B_9H_{11})_2$]} all show coordination chain structures. The carborane anions in {Ag(adiponitrile)[$Co(C_2B_9H_{11})_2$]} bridge between Ag centers to give a 3D $CdSO_4$-related coordination polymer. The structure of [Ag(malonitrile)$_2$](BF_4) was also determined to have an unusual chiral diamondoid structure with a skewed 2-fold interpenetration.

Introduction

Carboranes are C- and B-based cage cluster compounds with acidic C−H groups capable of forming hydrogen-bonding interactions.[1] Many carboranes are anionic in nature and are used as very weakly coordinating anions,[2] including the icosahedral monocarbaborane $(CB_{11}H_{12})^-$ and sandwich complexes such as cobalt(III) bis(dicarbollide), $[Co(C_2B_9H_{11})_2]^-$. Although regarded as weakly coordinating these types of carboranes may coordinate to Ag(I) through B−H$\cdots$Ag interactions[3−5] and halogenated carboranes coordinate to metal centers through the halide atoms.[6,7] The use of carboranes as anions in supramolecular chemistry is relatively unexplored, though a handful of examples are known. For example, the anions $(CB_{11}H_{12})^-$ and $[Co(C_2B_9H_{11})_2]^-$ have been utilized as simple counterions for coordination polymers,[8] for crystalline host−guest assemblies,[5,9] and for metallosupramolecular species.[10] Anions may also may form part of a coordination polymer through Ag$\cdots$H−B interactions.[4,5]

An important focus of crystalline supramolecular chemistry in recent years has been the area of coordination polymers or metal−organic frameworks.[11] Coordination polymers are infinite 1D, 2D, or 3D coordination complexes which, unlike many organic polymers, are highly ordered. Such materials may have substantial “empty” space where guest molecules or counterions can be included and, hence, have the potential for zeolitic applications. Coordination polymers are also significant from a structural chemistry perspective with new structural types being discovered as well as providing numerous examples of phenomena such as the interpenetration of networks.[12]

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(1) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970.

(2) Xie, Z.; Jelinek, T.; Bau, R.; Reed C. A. *J. Am. Chem. Soc*. **1994**, *116*, 1907.

(3) (a) Tsang, C.-W.; Sun, J.; Xie, Z. *J. Organomet. Chem.* **2000**, *613*, 99. (b) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955. (c) Ivanov, S. V.; Ivanova, S. M.; Miller, S. M.; Anderson, O. P.; Solntsev, K. A.; Strauss, S. H. *Inorg. Chem.* **1996**, *35*, 6914.

(4) (a) Patmore, N. J.; Hague, C.; Cotgreave, J. H.; Mahon, M. F.; Frost, C. G.; Weller, A. S. *Chem.*—*Eur. J.* **2002**, *8*, 2088. (b) Patmore, N. J.; Steed, J. W.; Weller, A. S. *Chem. Commun.* **2000**, 1055.

(5) Ahmad, R.; Hardie, M. J. *Cryst. Growth Des.* **2003**, *3*, 493.

(6) Ahmad, R.; Franken, A.; Kennedy, J. D., Hardie, M. J. *Chem.*—*Eur. J.* **2004**, *10*, 2190.

(7) (a) Tsang, C.-W.; Yang, Q.; Tung-Po Sze, E.; Mak, T. C. W.; Chan, D. T. W.; Xie, Z. *Inorg. Chem.* **2000**, *39*, 5851. (b) Tsang, C.-W.; Yang, Q.; Tung-Po Sze, E.; Mak, T. C. W.; Chan, D. T. W.; Xie, Z. *Inorg. Chem.* **2000**, *39*, 3582. (c) Evans, D. R.; Reed, C. A. *J. Am. Chem. Soc.* **2000**, *122*, 4660. (d) Patmore, N. J.; Ingleson, M. J.; Mahon, M. F.; Weller, A. S. *J. Chem. Soc., Dalton Trans.* **2003**, 2894.

(8) (a) Hardie, M. J.; Raston, C. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 3835. (b) Hardie M. J.; Raston, C. L. *Cryst. Growth Des.* **2001**, *1*, 53. (c) Long, D.-L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schröder, M. *Angew. Chem., Int Ed.* **2001**, *40*, 2444. (d) Malic, N.; Nichols, P. J.; Raston, C. L. *Chem. Commun.* **2002**, 16.

(9) (a) Hardie, M. J.; Malic, N.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **2002**, 295. (b) Hardie, M. J.; Raston, C. L. *Chem. Commun.* **2001**, 905.

(10) Schweiger, M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *Inorg. Chem.* **2002**, *41*, 2556.

(11) Braga, D.; Grepioni, F.; Orpen, A. G. *Crystal engineering: from molecules and crystals to materials*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1999.

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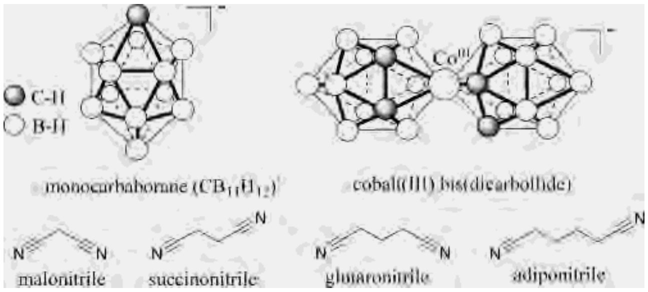
As part of a study of the supramolecular chemistry of carborane anions, we are investigating the use of the simple carborane anions $(CB_{11}H_{12})^-$ and $[Co(C_2B_9H_{11})_2]^-$ as counteranions for cationic coordination polymers that have been systematically characterized with other, more traditional, weakly coordinating anions. One such system is that of silver alkanedinitrile coordination polymers that have been well characterized by Ciani and co-workers with anions such as NO_3^-, BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, ClO_4^-, and $CF_3SO_3^-$.[13-15] Two distinct topologies have emerged from these studies, diamondoid 3D networks of 6^6 topology and 2D square layers. Interpenetrating diamondoid networks occur for $[Ag(dinitrile)_2]^+$ complexes with ligands 1,4-butanedinitrile (succinonitrile), 1,6-hexanedinitrile (adiponitrile),[14] 1,10-decanedinitrile (sebacodinitrile),[15] and 1,12-dodecanedinitrile.[13] The anion appears to have little influence on the network topology with the exception of $[Ag(adiponitrile)_2](ClO_4)$, which has a 2D square structure,[16] and sebacodinitrile complexes, where 3D diamondoid, 3D $SrAl_2$-type and 2D layers were observed.[13] Diamondoid structures were only obtained when the alkane chain had an even number of carbon atoms. Other dinitrile ligands, 1,5-pentanedinitrile (glutaronitrile), 1,7-heptanedinitrile (pimelonitrile), 1,8-octanedinitrile (suberonitrile), and 1,9-nonanedinitrile (azelanitrile), favor 2D layer structures.[14] Chain structures of composition $[Ag(dinitrile)](CF_3SO_3)$ have also been reported for adiponitrile and azelanitrile where the triflate anions interact weakly with the Ag metal centers.[15]



We report herein complexes of Ag(I) and alkanedinitriles $NC-(CH_2)_n-CN$, with $n = 1-4$, with the carborane counteranions $(CB_{11}H_{12})^-$ and $[Co(C_2B_9H_{11})_2]^-$. The common structural motifs previously reported for such silver dinitrile complexes, diamondoid and 2D layers, were not observed. New types of structures with either discrete, chain, or 3D lattice structures were observed. In most cases the counteranion interacts with Ag(I) centers through B−H···Ag interactions. We also report the complex $[Ag(malonitrile)_2](BF_4)_2$, which has a chiral 2-fold interpenetrating diamondoid structure with an unusual skewed mode of interpenetration, and is an anomaly to Ciani's observations that diamondoid structures are favored by an alkanedinitrile with an even number of carbon atoms.

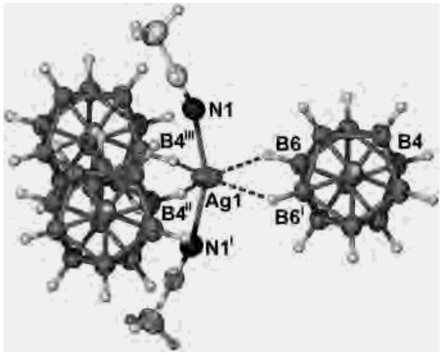


Figure 1. Silver coordination environment for $[Ag(acetonitrile)_2(CB_{11}H_{12})]$, **1**. Dashed lines indicate long B−H···Ag interactions. Ellipsoids are shown at 50% probability. Symmetry operations: i, $-x$, y, $0.5 - z$; ii, $x - 0.5$, $y - 0.5$, z; iii, $0.5 - x$, $y - 0.5$, $0.5 - z$.

Results and Discussion

Solutions of $Ag(CB_{11}H_{12})$ or $Ag[Co(C_2B_9H_{11})_2]$ with alkanedinitriles $NC(CH_2)_nCN$, where $n = 1-4$, where mixed in 1:1 and 1:2 proportions in a variety of solvents and allowed to slowly evaporate. Use of the smaller $(CB_{11}H_{12})^-$ anion gave crystals of suitable quality for single-crystal X-ray diffraction studies for a 1:2 metal:ligand complex with malonitrile and a 1:1.25 complex with succinonitrile. The larger $[Co(C_2B_9H_{11})_2]^-$ anion gave crystals of suitable quality for 1:2 and 1:1 complexes with glutaronitrile and a 1:1 complex with adiponitrile. All structures were determined by single-crystal X-ray diffraction techniques, and a summary of the data collections and structure refinements is given in Table 1. As a comparison, the structure of $Ag(CB_{11}H_{12})$ with the simplest of nitrile ligands, acetonitrile, was also determined. The corresponding $[Co(C_2B_9H_{11})_2]^-$ complex $\{Ag(NCCH_3)_2[Co(C_2B_9H_{11})_2]\}$ has been previously reported,[5] where a coordination chain is formed through B−H···Ag interactions.

$[Ag(CH_3CN)_2(CB_{11}H_{12})]$, 1. Colorless crystals of **1** were grown from an acetonitrile/trifluoroethanol solutions of $Ag(CB_{11}H_{12})$. Complex **1** undergoes a phase change at around 156(1) K which results in the formation of a crystalline powder that could not be characterized by single-crystal techniques. Hence, the X-ray diffraction data for **1** were collected at 200(1) K, which is well above the phase transition temperature. The silver coordination environment is shown in Figure 1, and bonds lengths and angles are given in Table 2. The silver is linearly coordinated by two crystallographically equivalent acetonitrile ligands at the Ag−N distance 2.172(5) Å and N−Ag−N angle of 157.6(2)°. There are four additional interactions to B−H groups of three surrounding $(CB_{11}H_{12})^-$ anions at B−H···Ag distances 2.421 and 2.405 Å forming a distorted octahedral coordination environment. B−H···Ag interactions have been previously documented for carborane anions,[3-5] though these distances are long, indicating a weak interaction. The silver coordination environment of **1** is similar to that of the analogous cobalt(III) bis(dicarbollide)

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(12) Batten, S. R. *CrystEngComm* **2001**, *3*, 67.

(13) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M.; Rizzato, S. *Chem.—Eur. J.* **1999**, *5*, 237.

(14) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *CrystEngComm* **2002**, *4*, 413.

(15) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *Chem.—Eur. J.* **2002**, *8*, 1520.

(16) Barnhart, D. M.; Caughlan, C. N.; Hauque, M. U. *Inorg. Chem.* **1969**, *8*, 276.

Table 1. Details of X-ray Data Collection and Structure Refinement for **1**−**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
formula	$C_5H_{18}AgB_{11}N_2$	$C_7H_{16}AgB_{11}N_4$	$C_{36}H_{102}Ag_6B_{66}N_{15}$	$C_{28}H_{68}Ag_2B_{36}Co_2N_8$	$C_9H_{28}AgB_{18}CoN_2$	$C_{20}H_{60}Ag_2B_{36}Co_2N_4$	$C_{12}H_8Ag_2B_2F_8N_8$
M_r	332.99	383.02	2106.01	1239.66	525.71	1079.48	653.62
cryst color and shape	block, colorless	needle, colorless	fragment, colorless	needle, yellow-orange	plate, yellow-orange	fragment, yellow-orange	block, colorless
crysl size (mm)	0.26 × 0.23 × 0.20	0.59 × 0.20 × 0.17	0.33 × 0.26 × 0.11	0.63 × 0.20 × 0.13	0.20 × 0.13 × 0.07	0.49 × 0.13 × 0.07	0.46 × 0.30 × 0.30
cryst system	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1$	Cc	$P2_1$	$P2_12_12_1$
a (Å)	7.3475(2)	9.8553(1)	15.8940(2)	6.9479(1)	6.9226(1)	10.5596(1)	10.0144(1)
b (Å)	15.1122(3)	10.1320(1)	16.0933(2)	21.1986(2)	28.1357(5)	20.4064(2)	10.1260(1)
c (Å)	13.7108(3)	10.3829(1)	19.5732(3)	18.9244(2)	11.5220(2)	10.9089(1)	20.4363(3)
α (deg)	90	71.110(1)	68.002(1)	90	90	90	90
β (deg)	95.194(1)	64.613(1)	78.813(1)	93.987(1)	93.316(1)	95.368(1)	90
γ (deg)	90	62.074(1)	88.766(1)	90	90	90	90
V (Å^3)	1516.15(6)	817.71(1)	4546.6(1)	2780.55(6)	2240.41(6)	2340.38(4)	2072.36(4)
Z	4	2	2	2	4	2	4
T (K)	200	150	100	150	150	150	150
ρ_c (g cm^{-3})	1.459	1.556	1.538	1.481	1.559	1.532	2.095
F(000)	656	376	2070	1240	1040	1072	1248
μ (cm^{-1})	1.303	1.223	1.309	1.316	1.616	1.549	1.977
2θ range (deg)	3.08−27.44	2.59−28.53	1.41−22.50	2.89−27.49	2.29−27.46	2.57−27.49	1.99−27.52
no. of data collcd	9850	16 014	27 553	37 799	15 246	24 156	25 923
no. of unique data	1724	3736	11 856	12 207	4799	10 254	4707
R_{int}	0.1376	0.0682	0.145	0.067	0.070	0.0788	0.0904
no. of obsd data ($I > 2\sigma(I)$)	1507	3465	9542	11432	4476	9469	4455
no. of params	89	148	1135	686	280	577	289
no. of restraints	0	0	232	1	2	1	0
R_1 (obs. data)	0.0615	0.0444	0.1495	0.0353	0.0337	0.0410	0.0637
wR_2 (all data)	0.1752	0.1194	0.3767	0.1017	0.0903	0.1080	0.1976
S	1.101	1.043	0.989	1.090	1.048	1.028	1.272
Flack param				0.558(11)	−0.020(18)	−0.001(13)	0.06(8)

Table 2. Selected Interatomic Distances (Å) and Angles (deg)[a]

Complex 1			
Ag1−N1	2.172(5)	Ag1−H4	2.405
Ag1−H6	2.421		
N1−Ag1−N1	157.6(2)	H4−Ag1−H4	137.3
N1−Ag1−H6	91.7	H4−Ag1−H6	147.2
N1−Ag1−H6	106.1	H6−Ag1−H6	75.6
N1−Ag1−H4	83.6		
Complex 2			
Ag1−N1	2.189(3)	Ag1−N4	2.252(3)
Ag1−N3	2.492(3)	Ag1−H6	2.038
N1−Ag1−N4	132.81(11)	H6−Ag1−N1	121.88
N1−Ag1−N3	98.57(10)	H6−Ag1−N3	84.77
N4−Ag1−N3	93.92(10)	H6−Ag1−N4	104.41
Complex 4			
Ag1−N1	2.359(4)	Ag2−N4	2.240(3)
Ag1−N2	2.209(3)	Ag2−N5	2.245(3)
Ag1−N3	2.332(3)	Ag2−N6	2.347(4)
Ag1−N8	2.243(3)	Ag2−N7	2.370(3)
N1−Ag1−N2	102.09(13)	N4−Ag2−N5	131.69(13)
N1−Ag1−N8	110.56(13)	N4−Ag2−N6	117.85(13)
N2−Ag1−N1	102.09(13)	N4−Ag2−N7	95.52(12)
N2−Ag1−N3	95.56(12)	N5−Ag2−N6	98.33(13)
N2−Ag1−N8	130.25(12)	N5−Ag2−N7	111.56(12)
N3−Ag1−N8	95.56(12)	N6−Ag2−N7	96.97(12)
Complex 5			
Ag1−N1	2.160(3)	Ag1−H8	2.036
Ag1−N2	2.171(4)	Ag1−H17	2.118
N1−Ag1−N2	153.32(13)	N2−Ag1−H8	91.09
N1−Ag1−H8	113.32	N2−Ag1−H17	97.35
N1−Ag1−H17	96.46	H8[a]−Ag1−H18	82.44
Complex 6			
Ag1−N1	2.156(3)	Ag2−N4	2.130(3)
Ag1−N2	2.174(3)	Ag2−H12	2.472
Ag1−H11	2.160	Ag2−H29	2.312
Ag1−H21	2.493	Ag2−H34	2.573
Ag2−N3	2.151(4)		
N1−Ag1−N2	148.60(16)	N3−Ag2−H29	90.96
N1−Ag1−H11	106.09	N3−Ag2−H34	78.72
N2−Ag1−H11	104.93	N4−Ag2−H12	88.97
N1−Ag1−H21	92.53	N4−Ag2−H32	102.91
N2−Ag1−H21	87.52	N4−Ag2−H29	111.31
H11−Ag1−H21	83.94	H12−Ag2−H29	76.30
N3−Ag2−N4	157.33(14)	H12−Ag2−H34	149.76
N3−Ag2−H12	100.85	H29−Ag2−H34	73.49
Complex 7			
Ag1−N1	2.292(8)	Ag2−N4	2.250(8)
Ag1−N2	2.229(8)	Ag2−N5	2.280(9)
Ag1−N3	2.329(10)	Ag2−N6	2.279(8)
Ag1−N7	2.255(8)	Ag2−N8	2.257(9)
N1−Ag1−N3	103.5(3)	N4−Ag2−N5	109.4(3)
N2−Ag1−N1	108.2(3)	N4−Ag2−N6	104.7(3)
N2−Ag1−N7	125.0(3)	N4−Ag2−N8	123.5(3)
N2−Ag1−N3	108.4(3)	N6−Ag2−N5	104.5(4)
N7−Ag1−N1	105.9(3)	N8−Ag2−N5	106.8(3)
N7−Ag1−N3	103.9(3)	N8−Ag2−N6	106.3(3)

[a] All hydrogen atoms are in calculated positions.

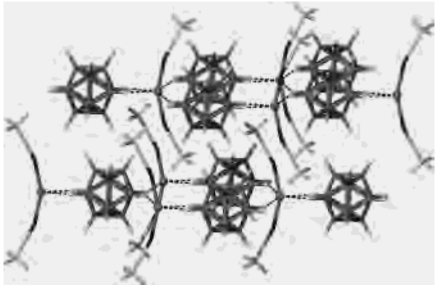

Figure 2. Packing of 2D coordination polymers of complex **1**.

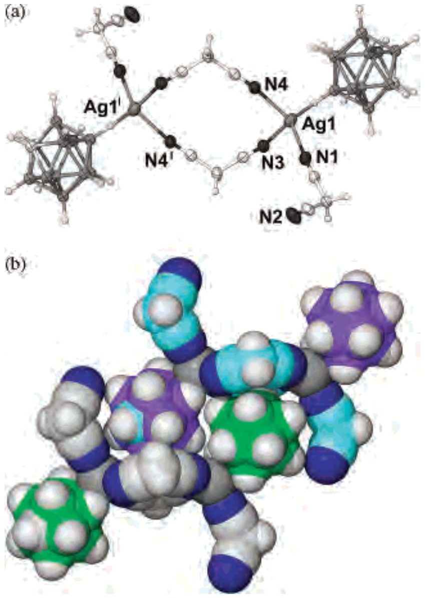

Figure 3. (a) Silver coordination environment of complex **2**. Ellipsoids are shown at 50% probability level. Symmetry operation: i, 2 − *x*, 2 − *y*, −*z*. (b) Association of two dimers. One dimer is shown with C in gray and B in green, and the other with C in light blue and B in purple.

complex $\{Ag(NCCH_3)_2[Co(C_2B_9H_{11})_2]\}$,[5] where a trigonal bipyramidal coordination environment is observed with axial acetonitrile ligands and equatorial B−H···Ag interactions with interatomic distances 2.35−2.56 Å.

Each $(CB_{11}H_{12})^-$ anion in complex **1** forms B−H···Ag interactions with three silver centers, and every silver center interacts with three $(CB_{11}H_{12})^-$ anions forming a 2D network structure of hexagonal 6^3 topology. These networks pack in the crystal lattice through interdigitation of the terminal acetonitrile ligands as shown in Figure 2. The closest N···N or N···B contacts between an acetonitrile of one network and acetonitrile or carborane of an adjacent network are around 4 Å.

$[Ag(NCCH_2CN)_2(CB_{11}H_{12})]$, 2. Crystals of $[Ag(malonitrile)_2](CB_{11}H_{12})$, **2**, were grown by slow evaporation of a 1:2 mixture of $Ag(CB_{11}H_{12})$ and malonitrile in ethanol. Complex **2** crystallizes in a triclinic cell, and the structure was solved in space group $P\bar{1}$. The asymmetric unit consists of one silver center, two malonitrile ligands, and one $(CB_{11}H_{12})^-$ counteranion. The silver center has a distorted tetrahedral geometry, Figure 3a, with coordination by three malonitrile nitrogen atoms and one B−H···Ag interaction. Bond lengths and angles are given in Table 2. The B−H···Ag interatomic distance is 2.038 Å, consistent with previously reported close B−H···Ag bonding distances of the order 2−2.2 Å.[3,4]

The complex is a discrete dimeric complex. There are two types of malonitrile ligand. One type of ligand bridges between two Ag centers to form a cyclic dimer with a Ag···Ag separation of 7.39 Å, Figure 3a. The other coordinates in a terminal fashion with a pendant nitrile group

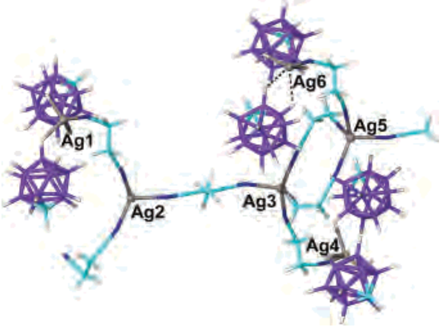

Figure 4. Idealized asymmetric unit of the crystal structure of $[Ag_4(succinonitrile)_5(CB_{11}H_{12})_4]$, **3**. The refined model has Ag4−Ag6 and one N disordered over two positions; however, an averaged position is shown for each to improve clarity. Dashed lines indicate long B−H···Ag interactions.

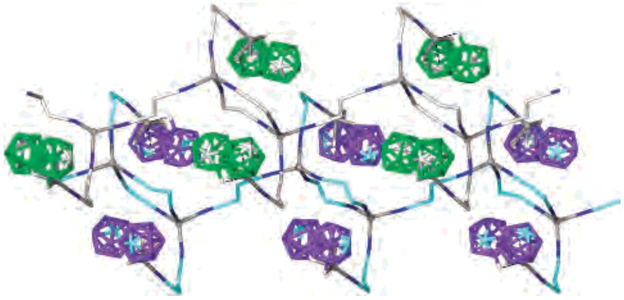

Figure 5. Packing of adjacent coordination chains from the crystal structure of complex **3**. One chain is shown with C in gray and B in green, and the other with C in light blue and B in purple.

that is not involved in coordination nor shows any close hydrogen-bonding contacts with adjacent dimers. Viewed side-on the $[(NCCH_2CN{-}Ag\text{-}\mu\text{-}(NCCH_2CN)_2{-}Ag{-}(NCCH_2CN)]$ fragment has a S-shaped configuration with the two terminal malonitrile ligands pointing in opposite directions. The dimers pack together in a linear fashion with the $(CB_{11}H_{12})^-$ moiety of one complex perched above the $Ag\text{-}\mu\text{-}(NCCH_2CN)_2{-}Ag$ cyclic fragment of an adjacent complex. Two such complexes are illustrated in Figure 3b, though in the extended structure a $(CB_{11}H_{12})^-$ anion is perched on both sides of the cyclic fragment, giving a ribbon motif. This packing motif between the complexes brings the molecules close together with the distance between the center of the $Ag{-}\mu\text{-}(NCCH_2CN)_2{-}Ag$ cyclic fragment and the closest B−H group of only 1.78 Å (corresponding B···center distance 2.82 Å). The overall three-dimensional crystal structure is composed of parallel ribbons slightly displaced from one another.

$[Ag_4(NC(CH_2)_2CN)_5(CB_{11}H_{12})_4]$, 3. Colorless crystals of $[Ag_4(succinonitrile)_5(CB_{11}H_{12})_4]$, **3**, were grown from the slow evaporation of an ethanol solution of $[Ag(CB_{11}H_{12})]$ and succinonitrile in 1:2 proportions. Complex **3** crystallizes in a triclinic cell, and the structure was solved in space group $P\bar{1}$. Crystals were of poor quality, and the structure solution shows significant disorder with three of the Ag atoms each disordered over two sites. Despite this the structural features of complex **3** can be elucidated, although geometric parameters, especially around the disordered Ag sites, should be regarded as approximate. The asymmetric unit of complex **3** is shown in Figure 4, with disordered atoms (Ag4, Ag5, Ag6, and N10) shown at averaged positions for clarity. There are six Ag centers, six $(CB_{11}H_{12})^-$ anions, and seven and a half succinonitrile ligands in the asymmetric unit.

The Ag centers fall into two groups, either coordinated by four succinonitrile ligands (Ag2, Ag3, Ag5) or by one succinonitrile ligand and two $(CB_{11}H_{12})^-$ anions (Ag1, Ag4, Ag6). The first type of Ag center propagates a coordination chain. All have distorted tetrahedral geometry with Ag−N distances ranging from 2.194 to 2.350(9) Å and N−Ag−N angles ranging from 97.8 to 121.3(3)°.[17] Each of these Ag centers is connected to two others of the same type through bridging succinonitrile ligands, to give a coordination chain shown in Figure 5. Bridging between Ag centers within the chain alternates between a single succinonitrile bridge and a double succinonitrile bridge. The double bridging creates cyclic $Ag{-}\mu\text{-}(NC(CH_2)_2CN)_2{-}Ag$ fragments throughout the chain, similar to the cyclic $Ag{-}\mu\text{-}(NCCH_2CN)_2{-}Ag$ fragment of the discrete complex **2**.

Ag centers of the other type are not involved in propagating the chain structure but are effectively terminal branches from the chain. Each is connected to the chain via a single bridging succinonitrile, and the other coordination sites are occupied by B−H···Ag interactions. For Ag1, the coordination environment is distorted tetrahedral with three B−H···Ag bonds at distances 1.971, 2.062, and 2.139 Å. There are two close B···N distances at 2.572(11) and 2.607(13) Å. The coordination environment around Ag4 is very similar to that of Ag1, while for Ag6 the environment shows two short B−H···Ag interactions and two long B−H···Ag interactions at around 2.5 Å. The terminal branches occur on either side of the coordination chain and curve inward. This results in one of the coordinated $(CB_{11}H_{12})^-$ anions from each terminal Ag being positioned directly over a cyclic $Ag{-}\mu\text{-}(NC(CH_2)_2CN)_2{-}Ag$ fragment, with one on each side of the cyclic fragment. This is remarkably similar to the packing motif found for complex **2**, but here the motif is intra- rather than intermolecular. The molecular fragments have a marginally closer approach in this intramolecular example with the distance between the center of the $Ag{-}\mu\text{-}(NC(CH_2)_2CN)_2{-}Ag$ cyclic fragments and the closest B−H groups ranging from 1.66 to 1.74 Å with corresponding B···center distances 2.69−2.78 Å. The coordination chains pack together through a simple translation as shown in Figure 5. The Ag···Ag separation between the chains is ~4 Å, which is too long to indicate a significant metallophilic interaction between the chains.[18]

$[Ag(NC(CH_2)_3CN)_2][Co(C_2B_9H_{11})_2]$, 4. Yellow-orange crystals of $[Ag(glutaronitrile)_2][Co(C_2B_9H_{12})_2]$, **4**, were obtained from the slow evaporation of an ethanol solution of $Ag[Co(C_2B_9H_{11})_2]$ and glutaronitrile in 1:2 proportions. Complex **4** crystallizes in a monoclinic cell, and the structure was solved in the chiral space group $P2_1$. There are two Ag

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(17) Quoted interatomic distances are to the averaged position of the two disordered Ag sites and, hence, should be regarded as approximate.

(18) Examples of metallophilic attraction: (a) Chen, C.-H.; Feng, X.-L.; Chen, X.-M. *Polyhedron* **2002**, *21*, 689. (b) Driess, M.; Faulhaber, M.; Merz, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2192.

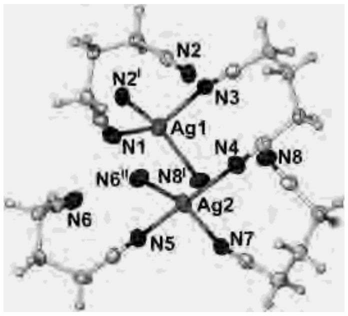

Figure 6. Silver coordination environment of [Ag(glutaronitrile)$_2$][Co($C_2B_9H_{11}$)$_2$], **4**. Ellipsoids are shown at 50% probability. Symmetry operations: i, 1 + *x*, *y*, *z*; ii, *x* − 1, *y*, *z*.

centers, four glutaronitrile ligands, and two [Co($C_2B_9H_{11}$)$_2$]$^-$ counteranions in the asymmetric unit. Both Ag centers are coordinated by glutaronitrile ligands with distorted tetrahedral geometries, Figure 6. Coordination distances and angles for both Ag centers are given in Table 2 with Ag−N distances ranging from 2.209(3) to 2.370(3) Å and N−Ag−N angles from 95.52(12) to 130.25(12)°.

Each glutaronitrile ligand bridges between two silver centers to give a [Ag(glutaronitrile)$_2$] coordination chain with a criss-crossed ladder topology, Figure 7a. The ladder is of unusual topology for a 4-connected polymer, and the Ag···Ag separations within the ladder are 6.95 Å along the sides and 4.52 Å along the zigzagging struts. The conformation of the bridging glutaronitrile ligands differs according to whether they bridge along the ladder sides or struts. The side bridges have a staggered conformation while the struts have a U-shaped eclipsed conformation. [Ag(glutaronitrile)$_2$]$^+$ coordination chains do not show any close interactions with the [Co($C_2B_9H_{11}$)$_2$]$^-$ anions, and the crystal packing shows isolated coordination chains and double columns of [Co($C_2B_9H_{11}$)$_2$]$^-$ anions in the arrangement as shown in Figure 7b. Coordination chains within the crystalline lattice are related to one another by the 2-fold screw axis.

{**Ag(NC(CH$_2$)$_3$CN)[Co($C_2B_9H_{11}$)$_2$]**}, **5.** Yellow-orange crystals of {Ag(glutaronitrile)[Co($C_2B_9H_{11}$)$_2$]}, **5**, were obtained from the slow evaporation of an ethanol solution of Ag[Co($C_2B_9H_{11}$)$_2$] and glutaronitrile in 1:1 proportions. The complex crystallizes in a monoclinic cell and the structure was solved in space group *Cc*. The asymmetric unit is composed of one silver center, one glutaronitrile ligand, and one [Co($C_2B_9H_{11}$)$_2$]$^-$ anion. The silver coordination environment of complex **5** is shown in Figure 8, with bond lengths and angles given in Table 2. The silver center has two glutaronitrile ligands at Ag−N distances 2.160(3) and 2.171(4) Å and two close B−H···Ag agostic interactions at 2.036 and 2.118 Å. The corresponding B···Ag distances are not close however at 2.90 and 3.05 Å. The glutaronitrile ligands deviate from linearity with an N−Ag−N angle of 153.32(13)°. The B−H···Ag interactions come from a single η^2-[Co($C_2B_9H_{11}$)$_2$]$^-$ anion and run roughly perpendicular to the N−Ag−N axis, to form a silver coordination environment that can be regarded as a distorted T-shape. A symmetry-related [Co($C_2B_9H_{11}$)$_2$]$^-$ anion is positioned above the silver center, but with B−H···Ag distances 2.825 Å (H1) and 2.974 Å (H6) it is too far away to be regarded as part of the silver coordination sphere. The glutaronitrile ligand in complex **5** bridges between two symmetry-equivalent silver centers, and a single-stranded coordination chain is propagated, Figure 9. The coordination chains pack through simple translations in the *a* and *b* directions, giving a polar overall crystal lattice.

{**Ag(NC(CH$_2$)$_4$CN)[Co($C_2B_9H_{11}$)$_2$]**}, **6.** Yellow-orange crystals of {Ag(adiponitrile){Co($C_2B_9H_{11}$)$_2$]}, **6**, were obtained by the slow evaporation of an ethanol solution of Ag[Co($C_2B_9H_{11}$)$_2$] and adiponitrile in 1:1 proportions. Complex **6** crystallizes with a monoclinic cell, and the structure was solved in the chiral space group $P2_1$. The asymmetric unit comprises two silver centers, two adiponitrile ligands, and two [Co($C_2B_9H_{11}$)$_2$]$^-$ anions. Selected bond lengths and angles are given in Table 2. As for the likewise 1:1 silver: dinitrile complex **5**, each silver center is coordinated by two adiponitrile ligands with a distorted linear geometry. Ag−N distances range from 2.151(4) to 2.174(3) Å, and N−Ag−N angles are 148.60(16) and 157.33(14)°. There is one close B−H···Ag interaction to Ag1 at a distance 2.160 Å and a further long interaction at B−H···Ag distance 2.49 Å. The geometry around Ag1 is best described as distorted trigonal

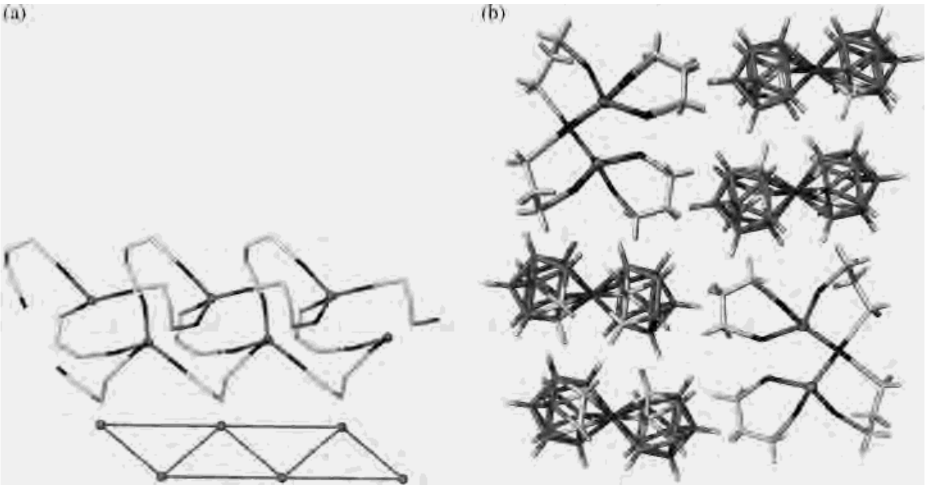

Figure 7. Extended structure of complex **4**: (a) [Ag(glutaronitrile)$_2$] chain with the topological Ag-to-Ag connectivity shown below; (b) packing of coordination chains and [Co($C_2B_9H_{11}$)$_2$]$^-$ anions.

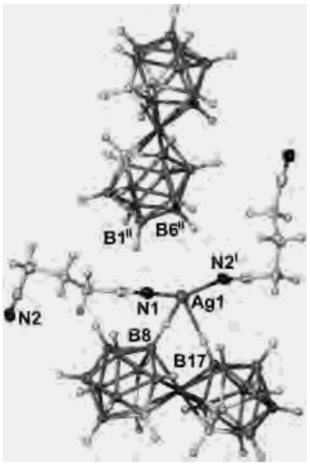

Figure 8. Silver coordination environment of {Ag(glutaronitrile)[Co($C_2B_9H_{11}$)$_2$]}, **5**. The close approach of a symmetry-related [Co($C_2B_9H_{11}$)$_2$]$^-$ is illustrated. Ellipsoids are shown at 50% probability. Symmetry operations: i, $x - 1$, $1 - y$, $0.5 + z$; ii, x, $1 - y$, $0.5 + z$.

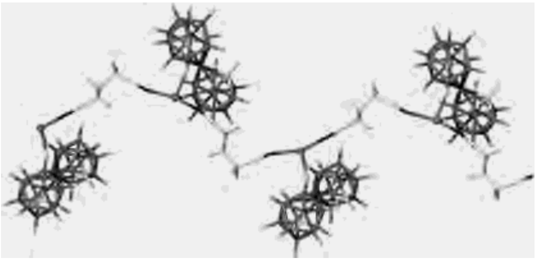

Figure 9. Coordination chain of complex **5**.

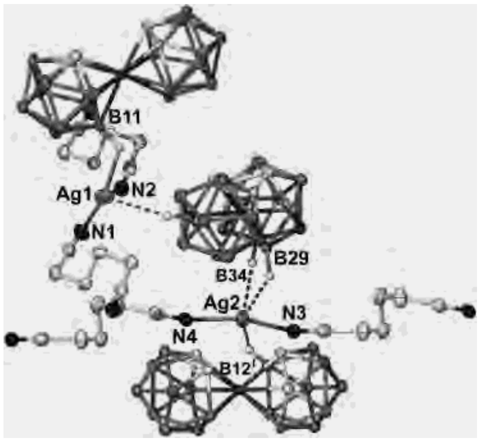

Figure 10. Silver coordination of {Ag(adiponitrile)[Co($C_2B_9H_{11}$)$_2$], **6**. Long B−H···Ag interactions are shown as dashed lines. Only hydrogen atoms involved in B−H···Ag interactions are shown for the sake of clarity. Ellipsoids are shown at 50% probability. Symmetry operation: i, $1 - x$, $0.5 + y$, $-z$.

pyramidal. This leaves one face of the silver uncoordinated, and the closest approach to this site is from a [Co($C_2B_9H_{11}$)$_2$]$^-$ anion at B−H···Ag distance greater than 3 Å. There are three long B−H···Ag interactions to Ag2 at distances ranging from 2.31 to 2.57 Å, with overall distorted trigonal bipyramidal geometry around Ag2, Figure 10.

Each adiponitrile ligand bridges between two symmetry-related silver centers to propagate a simple coordination chain. These chains run in two directions through the structure, either along the crystallographic *a* or *c* directions. The orientation of the chain alternates along the *b* direction.

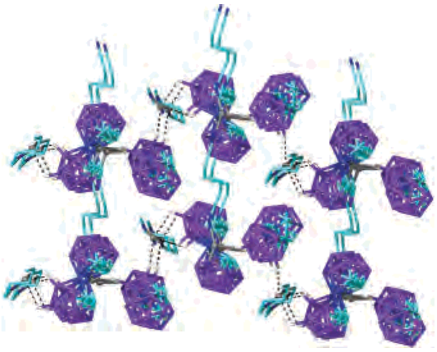

Figure 11. Extended structure of complex **6** with long B−H···Ag interactions shown as dashed lines.

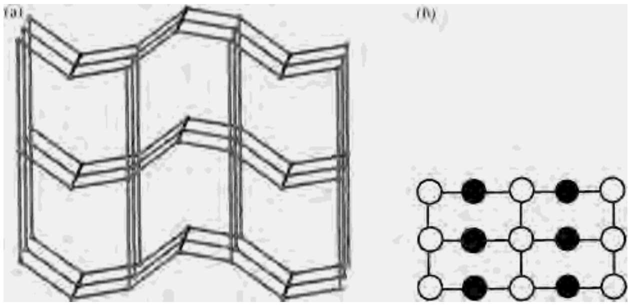

Figure 12. Topology of complex **6**: (a) Ag-to-Ag connectivity showing wavy 6^5.8 topology; (b) idealized $CdSO_4$ topology with shaded circles representing nodes which connect to an identical 2D network above and below the plane.

The combined strong and weak B−H···Ag interactions in **6** mean that each [Co($C_2B_9H_{11}$)$_2$]$^-$ anion bridges between two perpendicular chains creating a 3D coordination polymer, Figure 11. The Ag-to-Ag connectivity of **6** is shown in Figure 12a and reveals parallel wavelike sheets connected above and below in a linear fashion. The network is 4-connected with 6^5.8 topology and is identical with that of $CdSO_4$. The ideal $CdSO_4$ net is shown schematically in Figure 12b and features square planar connecting nodes, where each node connects to two others in the same orientation and two at 90° twist. The most common 4-connected network structure for coordination polymers is a diamondoid net with 6^6 topology;[19] in contrast, there are very few documented examples of coordination polymers with a $CdSO_4$ related topology.[20]

The use of the carborane anions has a marked effect on the type of coordination complex that is produced. Studies by Ciani et al. showed that succinonitrile and adiponitrile form [Ag(dinitrile)$_2$]$^+$ complexes that have interpenetrating diamondoid structures with a range of weakly coordinating anions. Adiponitrile may also form a 1:1 complex where a

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(19) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, 283.

(20) (a) Goodgame, D. M. L.; Grachvogel, D. M.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2001**, *40*, 6180. (b) Brooks, N. R.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Teat, S. J.; Wilson, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2001**, 2530. (c) Jiang, Y.-C.; Lai, Y.-C.; Wang, S.-L.; Lii, K.-H. *Inorg. Chem.* **2001**, *40*, 5320. (d) Long, D.-L.; Blake, A. J.; Champness, N. R.; Schröder, M. *Chem. Commun.* **2000**, 1369. (e) Plater, M. J.; Foreman, M. R. St. J.; Gelbrich, T.; Hursthouse, M. B. *Cryst. Eng.* **2001**, *4*, 319. (f) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M. *Chem. Commun.* **1998**, 1837. (g) Shin, D. M.; Lee, I. S.; Chung, Y. K.; Lah, M. S. *Chem. Commun.* **2003**, 1036. (h) Moulton, B.; Abourahma, H.; Bradner, M. W.; Lu, J.; McManus, G. J.; Zaworotko, M. J. *Chem. Commun.* **2003**, 1342.

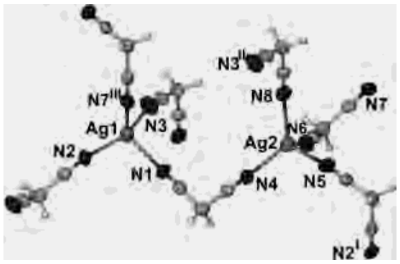

Figure 13. Silver coordination environment from the X-ray structure of $[Ag(malonitrile)_2](BF_4)$, **7**. Ellipsoids are shown at 50% probability. Symmetry operations: i, $0.5 - x$, $1 - y$, $z - 0.5$; ii, x, $1 + y$, z; iii, $-x - 0.5$, $1 - y$, $0.5 + z$.

$[Ag(adiponitrile)]^+$ coordination chain is linked into a 3D network by weak interactions from a $CF_3SO_3^-$ anion.[14] Complexes of $[Ag(glutaronitrile)_2]^+$ form a 2D square grid network with a range of weakly coordinating anions. The coordination polymers found with carborane anions were quite different. No diamondoid networks were observed despite there being sufficient space to accommodate the smaller $(CB_{11}H_{12})^-$ within the cavities of a noninterpenetrated diamondoid network with a long chain alkanedinitrile. Nor was the 2D square grid structure observed. Instead coordination chains predominate, and isolated crystalline complexes tended to have a Ag:dinitrile ratio of less than 1:2. In these cases the Ag(I) coordination sphere was completed by B−H···Ag interactions. In the case of complex **6** the anion acted as a bridging ligand linking $[Ag(adiponitrile)]^+$ chains into a 3D network, but in other cases the interactions to the anion were effectively terminal. Two 1:2 complexes were isolated, $[Ag(malonitrile)_2](CB_{11}H_{12})$, **2**, with a discrete dinuclear structure which again showed B−H···Ag interactions, and $[Ag(glutaronitrile)_2][Co(C_2B_9H_{11})_2]$, **4**, where there were no interactions to the anion, but nevertheless a chain structure was formed. As there are no B−H···Ag interactions in **4**, the formation of a chain structure rather than the previously reported 2D grid structure can be attributed to the steric influence of the large $[Co(C_2B_9H_{11})_2]^-$ anion.

$[Ag(NCCH_2CN)_2](BF_4)$, 7. $[Ag(malonitrile)_2]^+$ complexes have not been previously reported; hence, we investigated this system with BF_4^- which is one of the more common weakly coordination anions. Crystals of $[Ag(malonitrile)_2](BF_4)$, **7**, were grown by slow evaporation of a 1:2 mixture of $AgBF_4$ and malonitrile in aqueous ethanol solution. The structure was determined by single-crystal diffraction techniques. Complex **7** crystallizes with an orthorhombic unit cell, and the structure was solved in the chiral space group $P2_12_12_1$. There are two silver centers, four malonitrile ligands, and two BF_4^- counteranions in the asymmetric unit. Each Ag center has a distorted tetrahedral geometry, with four malonitrile ligands at Ag−N distances ranging from 2.229(8) to 2.329(10) Å, Figure 13. Selected bond angles and distances are given in Table 2.

Each malonitrile ligand bridges between two silver centers, propagating the 3D coordination polymer shown in Figure 14. The topology of the network as represented by the Ag-to-Ag connectivity is a 6^6 diamondoid structure. Interestingly this result is not in agreement with the previous observation that diamondoid networks tend to occur with dinitrile ligands having an even number of carbon atoms in the chain.[13−15] The short chain length of the malonitrile ligand may not favor the alternative 2D grid structure, where increased flexibility of the ligand may be important. The network of **7** is one of the few known examples of a chiral diamondoid structure.[21−24] The chirality can be easily appreciated from Figure 14, where helical channels of rectangular cross-section are evident. These helices run throughout the structure in one of two directions, aligned either parallel with the crystallographic *a* or *b* axis. Each parallel helix is of the same hand. The structure of diamond itself is not chiral as all links between tetrahedral C centers are straight. The chirality of this diamondoid network is a result of the kinked nature of the malonitrile ligand linking the tetrahedral Ag centers. Notably, malonitrile is not in itself chiral and the chirality of the complex is a function of the overall assembly. Chirality in a diamondoid network may arise from employing a kinked ligand,[21] an unsymmetrical ligand[22] or ligand binding modes[23] or usinga chiral building block.[24] Some chiral diamondoid coordination polymers have been shown to have interesting optical properties.[21,22]

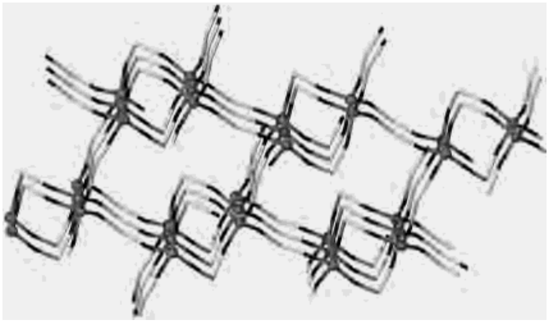

Figure 14. Single network of **7**. Channels with rectangular a cross section are helical and run exactly parallel with the same hand throughout the structure.

Complex **7** does not show a single diamondoid network but is 2-fold interpenetrating with a second identical network entangled in the first, Figure 15. The helical channels of the two interpenetrating networks are parallel to one another and have the same hand in each direction, preserving the overall chirality of the material. The interpenetration shown by complex **7** is unusual. In a normal mode of 2-fold interpenetration a connecting node of one network would be at the center of an adamantane-shaped cavity of the first and the two networks related by translation. Here the two networks are still related by a translation; however, the second network is not centered on the first. Rather it is skewed to one side, with a connecting Ag(I) node of the second network displaced around 6 Å from the center of the adamantane-shaped cavity of the first, Figure 15b. While 2-fold inter-

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(21) Chen, Z.-F.; Xiong, R.-G.; Abrahams, B. F.; You, X.-Z.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 2453.

(22) Xiong, R.-G.; Zuo, J.-L.; You, X.-Z.; Bai, Z.-P.; Abrahams, B. F.; Che, C.-M.; Fun, H.-K. *Chem. Commun.* **2000**, 2061.

(23) Blake, A. J.; Champness, N. R.; Cooke, P. A.; Nicolson, J. E. B.; Wilson, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3811.

(24) (a) Sauriat-Dorizon, H.; Maris, T.; Wuest, J. D.; Enright, G. D. *J. Org. Chem.* **2003**, *68*, 240. (b) Kostyanovsky, R. G.; Lyssenko, K. A.; Lenev, D. A.; Bronzova, I. A. *Tetrahedron: Asymmetry* **2002**, *13*, 2697.

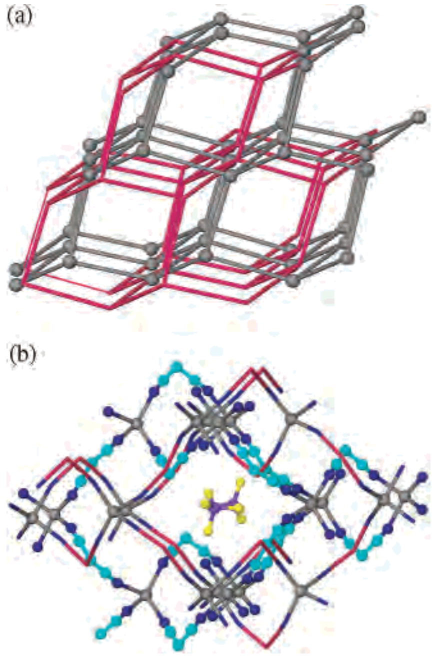

Figure 15. (a) Ag-to-Ag connectivity showing the 2-fold interpenetrating diamondoid structure of **7**. (b) Detail from the X-ray structure showing two interpenetrating adamantoid cages and BF_4^- anions.

penetrating diamondoid networks are quite common, this skewed mode of interpenetration has not been documented.[12] Unusual modes of interpenetration have been reported for diamondoid $[Ag(dinitrile)_2]^+$ coordination polymers with considerably longer dinitrile hydrocarbon chains.[15] The skewed interpenetration mode still preserves the square channels that are a feature of diamondoid networks and that frequently contain any counterions. For complex **7** these square channels are filled by the kinked malonitrile ligands and the BF_4^- anions are instead contained within cavities formed by network packing. This is an efficient packing mode, as evidenced by the high calculated density of complex **7** at 2.095 g cm^{-3}.

Use of the $(CB_{11}H_{12})^-$ anion in place of BF_4^- does not lead to a diamondoid structure. While this can be attributed to the coordination of the $(CB_{11}H_{12})^-$ anion seen in $[Ag(malonitrile)_2](CB_{11}H_{12})$, **2**, the kinked nature of the malonitrile ligand mean that the ligand $-CH_2-$ groups fill much of the space with the adamantane-shaped cavities of a diamondoid network and a $(CB_{11}H_{12})^-$ anion would be simply too large to fit.

Conclusion

The use of carborane as counteranion for coordination complexes formed by silver with alkanedinitriles has a marked effect on the structure and topology of complexes formed. The previously reported diamondoid and 2D square grid structures were not observed. This can be attributed to both the steric influence of the large anions and their tendency to form $B-H\cdots Ag$ interactions. The longer chain alkanedinitriles glutaronitrile and adiponitrile did not give crystalline complexes with $Ag(CB_{11}H_{12})$, while the shorter chain malonitrile and succinonitrile did not give crystalline complexes with $Ag[Co(C_2B_9H_{11})_2]$. When combined with the alkanedinitrile ligands malonitrile and succinonitrile $Ag(CB_{11}H_{12})$ forms coordination complexes with related structures. $[Ag(malonitrile)_2](CB_{11}H_{12})$ is a discrete dimeric complex with a cyclic $[Ag(dinitrile)]_2$ core and terminal $(CB_{11}H_{12})^-$ ligands, and the dimers stack so that the $(CB_{11}H_{12})^-$ ligands perch above the cyclic core. In $[Ag(succinonitrile)_{1.25}(CB_{11}H_{12})]$ a similar cyclic $[Ag(dinitrile)]_2$ fragment is linked into chains and $(CB_{11}H_{12})^-$ ligands from the same chain are positioned over the cyclic fragment. $Ag[Co(C_2B_9H_{11})_2]$ and glutaronitrile forms coordination chains with a 1:1 or 1:2 silver:dinitrile ratio. The latter complex does not feature any $B-H\cdots Ag$ interactions. $[Ag(dinitrile)_2]^+$ coordination chains within $\{Ag(adiponitrile)[Co(C_2B_9H_{11})_2]\}$ are linked into a 3D lattice with $CdSO_4$-related topology by bridging $[Co(C_2B_9H_{11})_2]^-$ anions. Bridging of such chains by weakly coordinating anions has also been observed for $[Ag(adiponitrile)(CF_3SO_3)]$.[14] The diamondoid structure of $[Ag(malonitrile)_2](BF_4)$ is surprising given that previous studies had led to the suggestion that diamondoid structures are favored by alkane dinitriles with an even number of carbon atoms. Notably this material is chiral and augers well for creating potentially useful chiral materials from simple reagents.

Experimental Section

Synthesis. $Ag(CB_{11}H_{12})$ and $Ag[Co(C_2B_9H_{11})_2]$ were prepared by literature methods from their commercially available salts.[2] AR grade reagents were used without further purification. $Ag(CB_{11}H_{12})$ was recrystallized from acetonitrile$-CF_3CH_2OH$ to give colorless crystals of **1**. Single crystals of complexes **2**−**6** suitable for single-crystal X-ray analysis were obtained by mixing ethanol solutions of silver carborane salt with the appropriate alkanedinitrile and allowing a slow evaporation. Likewise single crystals of complex **7** were obtained from $AgBF_4$ and an excess of malonitrile mixed in a 95:5 ethanol/water solution. Complexes were characterized by microanalysis, infrared spectroscopy, and single-crystal X-ray crystallography. Complex **1** lost solvent on drying, while complex **4** grew from an initial oil and redissolved on washing; hence, these were not subjected to microanalysis. Complex **2** undergoes slight deterioration, evidenced by darkening due to colloidal silver formation, and gave low microanalytical results.

Microanalysis and selected infrared ν (cm^{-1}) data are as follows. IR for **1**: 2978, 2536 b ($B-H$), 2259 ($C\equiv N$), 1616, 1418, 1026, 717. IR for **2**: 2951, 2920, 2548 b ($B-H$), 2361 ($C\equiv N$), 2343 ($C\equiv N$), 2280 ($C\equiv N$), 1616, 1389, 1091, 1026, 719. Anal. Calcd for **3**: C, 20.53; H, 4.88; N, 9.97. Found: C, 20.35; H, 4.75; N, 9.55. IR for **3**: 2976, 2532 b ($B-H$), 2361 ($C\equiv N$), 2343 ($C\equiv N$), 2257 ($C\equiv N$), 1618, 1425, 1244, 1091, 1024, 717. IR for **4**: 2930, 2540 b ($B-H$), 2359 ($C\equiv N$), 2345 ($C\equiv N$), 2255 ($C\equiv N$), 1618, 1420, 1099, 983, 723. Anal. Calcd for **5**: C, 20.56; H, 5.37; N, 5.33. Found: C, 20.6; H, 5.35; N, 5.15. IR for **5**: 3038, 2569 ($B-H$), 2525 b ($B-H$), 22884 ($C\equiv N$), 2255 ($C\equiv N$), 1618, 1416, 1201, 1099, 1016, 723. Anal. Calcd for **6**: C, 22.25; H, 5.60; N, 5.19. Found: C, 22.45; N, 5.5; H, 5.1. IR for **6**: 2973, 2564 ($B-H$), 2533 ($B-H$), 2250 ($C\equiv N$), 1628, 1417, 1100, 985, 723. Anal. Calcd for **7**: C, 22.05; H, 1.23; N, 17.4. Found: C, 21.85; H, 1.35; N, 17.3. IR for **7**: 2915, 2379 ($C\equiv N$), 2267 ($C\equiv N$), 1615, 1448 b, 1198, 1090, 805, 648, 549.

X-ray Collections and Structure Determinations. Details of data collection and structure refinement for **1**−**7** are given in Table

1. Single crystals of **1**−**7** were mounted on a glass fiber under oil and X-ray data collected on a Nonius KappaCCD diffractometer with Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data were corrected for Lorenztian and polarization effects; absorption corrections were applied using multiscan methods. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically and hydrogen atoms included in geometrically estimated positions with a riding refinement. C positions within carborane cages were determined by examining displacement parameters and bond lengths, noting that C−C bond lengths are considerably shorter than those for C−B or B−B. In the absence of neutron diffraction data these assignments should be regarded as tentative.

For complex **1** the C position could not be distinguished and each vertex of the CB_{11} icosahedron was modeled as having $^1/_{12}$th C and $^{11}/_{12}$th B character.

The structure refinement of complex **3** gave high residuals due to a number of factors. The high R_{int} value despite low symmetry indicates that the crystals were of poor quality. They were weakly diffracting with data to $2\theta = 45°$ having $R_\sigma = 0.1737$; hence, the refinement has a poor data:parameter ratio. The structure showed significant levels of disorder with three of the six silver centers refined over two positions at 50% occupancy each and indications of disorder in some succinonitrile ligands and four $(CB_{11}H_{12})^-$ anions. One nitrile N was refined over two positions at 50% occupancy each, and restraints were placed on the geometry, interatomic distances, and displacement parameters of four $(CB_{11}H_{12})^-$ anions. Attempts to model additional split positions for succinonitrile and anion atoms did not lead to an improved refinement.

Complex **4** was refined as an inversion twin. Data were not merged, and there was no indication of any missing symmetry.

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Supporting Information Available: Crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

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