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Silver−Thioether Crown Complexes as Templates for the Synthesis of Extended Polyiodide Networks: Synthesis and X-ray Crystal Structures of $[Ag_2([15]aneS_5)_2]I_{12}$, $[Ag([18]aneS_6)]I_7$, $[Ag([18]aneS_6)]I_3$, and $[Ag([9]aneS_3)_2]I_5$[†]

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Silver(I) complexes of $[9]aneS_3$, $[15]aneS_5$, and $[18]aneS_6$ have been used as templates for the self-assembly of polyiodide ions. The complexes $[Ag_2([15]aneS_5)_2]I_{12}$, $[Ag([18]aneS_6)]I_7$, $[Ag([18]aneS_6)]I_3$, and $[Ag([9]aneS_3)_2]I_5$ have been synthesized and structurally characterized. In $[Ag_2([15]aneS_5)_2]I_{12}$ [$C_{10}H_{20}AgI_6S_5$, orthorhombic, space group $Pna2_1$ with $a = 21.688(4)$ Å, $b = 27.748(4)$ Å, $c = 8.623(2)$ Å, $Z = 8$], a discrete I_{12}^{2-} polyiodide anion describable as a $[2I^-{\cdot}5I_2]$ charge-transfer adduct is bound to two $[Ag([15]aneS_5)]^+$ cations by Ag−I bonds. I···S interactions contribute to build up an extended three-dimensional superstructure featuring spirals of I_{12}^{2-} and $[Ag([15]aneS_5)]^+$ ions alternating along the c axis. In $[Ag([18]aneS_6)]I_7$ [$C_{12}H_{24}AgI_7S_6$, trigonal, space group $R\bar{3}m$ with $a = b = c = 9.458(4)$ Å, $\alpha = \beta = \gamma = 103.79(3)°$, $Z = 1$], the Ag(I) complex cation is embedded in a unique three-dimensional polyiodide matrix in which I^- ions occupy the lattice points of a primitive rhombohedral lattice with one I_2 molecule bridging two I^- ions along each cell edge to give a pseudo-perovskite structure. $[Ag([18]aneS_6)]I_3$ [$C_{12}H_{24}AgI_3S_6$, monoclinic, space group $C2/m$ with $a = 18.5767(11)$ Å, $b = 11.9188(7)$ Å, $c = 5.2714(5)$ Å, $\beta = 95.634(9)°$, $Z = 2$] features discrete $[Ag([18]aneS_6)]^+$ cations and I_3^- in a columnar stacking arrangement. Using the $[Ag([9]aneS_3)_2]^+$ cation as template, an I_5^- salt has been obtained; this contrasts with the cubelike $[I_7^-]_\infty$ polyiodide array and I_3^- salt isolated with the $[Ag([18]aneS_6)]^+$ cation. In $[Ag([9]aneS_3)_2]I_5$ [$C_{12}H_{24}AgI_5S_6$, monoclinic, space group $C2/c$ with $a = 17.1117(12)$ Å, $b = 12.612(2)$ Å, $c = 14.016(2)$ Å, $\beta = 118.65(4)°$, $Z = 4$], I···S interactions contribute to an extended structure featuring polymeric successions of cations and I_5^- ions. The solid-state FT-Raman spectra of these polyiodides are discussed on the basis of their crystal structures.

Introduction

Among the halogens, I_2 shows the highest ability to catenate,[1] and a wide range of structural motifs has been identified for the resulting polyiodide ions. While there are numerous examples of small polyiodides, such as I_3^-, I_4^{2-}, and I_5^-, polyanions having general formula I^{n-}_{2m+n} (m = number of diiodine molecules, n = number of iodide anions) with higher diiodine content such as I_7^-,[2−8] I_8^{2-},[9−14] I_9^-,[15] I_{10}^{4-},[16] I_{12}^{2-},[17−19] I_{16}^{2-},[18,20] I_{16}^{4-},[21,22] I_{18}^{4-},[23] and I_{22}^{4-} [24] become increasingly rare as m and n increase. Even rarer are polyiodides of the type I_{6i-1}^{3-} (I_{29}^{3-}, $i = 5$)[25] or I_{6i+1}^{3-} (I_7^{3-}, I_{13}^{3-}, $i = 1$ and 2, respectively).[18,26] On the basis of structural data and spectro-

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[†] Abbreviations used in the text: $[9]aneS_3$ = 1,4,7-trithiacyclononane, $[15]aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane, and $[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane.

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(1) (a) Tebbe, K.-F. In *Polyhalogen cations and Polyhalide Anions. Homoatomic Rings, Chains and Macromolecules of Main-Group Elements;* Rheingold, A. L., Ed.; Elsevier: Amsterdam, 1977; p 551. (b) Coppens, P. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1982; p 333.

(2) (a) Betzel, C.; Hingerty, B.; Noltemeyer, M.; Weber, G.; Saenger, W.; Hamilton, J. A. *J. Inclusion Phenom.* **1983**, *1*, 181. (b) Hendixson, T. L.; ter Horst, M. A.; Jacobson, R. A. *Acta Crystallogr.* **1991**, *C47*, 2141.

(3) Poli, R.; Gordon, J. C.; Khanna, R. K.; Fanwick, P. E. *Inorg. Chem.* **1992**, *31*, 3165.

(4) Demartin, F.; Deplano, P.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Verani, G. *Inorg. Chem.* **1993**, *32*, 3694.

(5) Renner, M. W.; Barkigia, K. M.; Zhang, Y.; Medforth, C. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1994**, *116*, 8582.

(6) Junk, P. C.; MacGillivray, L. R.; May, M. T.; Robinson, K. D.; Atwood, J. L. *Inorg. Chem.* **1995**, *34*, 5395.

(7) Herbstein, F. H.; Reisner, G. M.; Schwotzer, W. *J. Inclusion Phenom.* **1985**, *3*, 173.

(8) (a) Havinga, E. E.; Wiebenga, E. H. *Acta Crystallogr.* **1958**, *11*, 733. (b) Hassel, O.; Hope, H. *Acta Chem. Scand.* **1961**, *15*, 407.

(9) Beno, M. A.; Geiser, U.; Kostka, K. L.; Wang, H. H.; Webb, K. S.; Firestone, M. A.; Carlson, K. D.; Nuñez, L.; Whangbo, M.-H.; Williams, J. M. *Inorg. Chem.* **1987**, *26*, 1912.

(10) Havinga, E. E.; Boswijk, K. H.; Wiebenga, E. H. *Acta Crystallogr.* **1954**, *7*, 487.

(11) Hon, P. K.; Mak, T. C. W.; Trotter, J. *Inorg. Chem.* **1979**, *18*, 2916.

(12) (a) Jircitano, J.; Mertes, K. B. *Inorg. Chem.* **1983**, *22*, 1828. (b) Jircitano, A. J.; Colton, M. C.; Mertes, K. B. *Inorg. Chem.* **1981**, *20*, 890.

(13) Brelière, C.; Carré, F.; Corriu, R.; Wong Chi Man, M. *J. Chem. Soc., Chem. Commun.* **1994**, 2333.

(14) (a) Behrens, U.; Breunig, H. J.; Denker, M.; Ebert, K. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 987. (b) Thomas, R.; Moore, F. H. *Acta Crystallogr.* **1981**, *B37*, 2153. (c) Tebbe, K.-F.; El Essawi, M.; Abd El Khalik, S. *Z. Naturforsch., Teil B* **1995**, *50*, 1429.

(15) (a) James, W. J.; Hach, R. J.; French, D.; Rundle, E. R. *Acta Crystallogr.* **1955**, *8*, 814. (b) Tebbe, K.-F. *Z. Kristallogr.* **1988**, *185*, 496.

(16) Bigoli, F.; Demartin, F.; Deplano, P.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *Inorg. Chem.* **1996**, *35*, 3194.

(17) Tebbe, K.-F.; Kavoosian, A. *Z. Naturforsch., Teil B* **1993**, *48*, 438.

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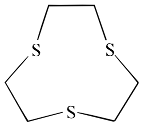
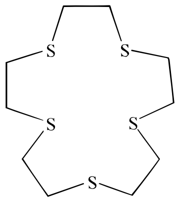
scopic studies,[27] all of these large polyiodide species can be considered as derived from the interaction of slightly elongated diiodine molecules (I−I ≈ 2.75−2.80 Å) with I_3^- and/or I^- ions, these interactions generally involving $(I_3^-)I^-\cdots I_2$ distances of 3.2−3.6 Å. Cross-linking distances via soft−soft secondary interactions generally range from 3.6 Å up to the van der Waals sum for two iodine atoms of 4.3 Å, and these are responsible for the formation of polymeric one-dimensional chains or extended two- or three-dimensional networks in the polyanionic matrix.[8,18,20,28] The apparently unpredictable structural and geometrical features of these polyiodide arrays are determined by the size, shape, and charge of the associated cation. Recently, we have been investigating the use of metal−thioether macrocyclic complexes as templating agents for controlling the structural features of extended polyiodide arrays.[29−31] Indeed, macrocyclic thioether complexes seem to be ideal reaction partners in the preparation of oligomeric anionic polyiodides since they are relatively chemically inert and their size, shape, and charge can be finely tuned by changing either the metal ion or the thioether ligand. Furthermore, as free ligands thioether macrocycles are known to form a wide range of charge-transfer adducts with I_2,[32] so that long-range S···I interactions may also participate in regulating solid-state organization in these complexes. We report herein the results achieved by using the Ag(I) complexes of [9]aneS_3, [15]aneS_5, and [18]aneS_6 as cationic partners for the template self-assembly of polyiodide anions.

Results and Discussion

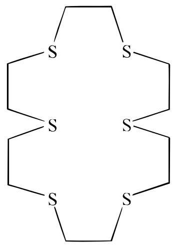
Synthesis and Structure. The coordination chemistry of Ag(I) with [9]aneS_3, [15]aneS_5, and [18]aneS_6 has already attracted some attention. The synthesis and structures of the complex cations $[Ag([9]aneS_3)_2]^+$ and $[Ag([18]aneS_6)]^+$ have been reported[33,34] and show octahedral Ag(I) with two [9]aneS_3 molecules bound facially to the metal center and one [18]aneS_6 ligand encapsulating the metal ion, respectively. In addition, with [9]aneS_3 an interesting trinuclear Ag(I) cation, $[Ag_3([9]aneS_3)_3]^{3+}$ incorporating bridging thioether ligands and metal ions coordinated to a highly distorted tetrahedral array of four S donors, has also been reported.[35] The effect of an inherent stereochemical mismatch between the coordination preferences of the Ag(I) ion (octahedral or tetrahedral) and the crown thioether (potentially three coordinate for [9]aneS_3) is even more evident with the potentially five-coordinate [15]aneS_5. Indeed, the structure of the $[Ag([15]aneS_5)]^+$ cation has been found to be heavily dependent upon the nature of the counteranion.[36] As our aim was to use metal thioether macrocycle complexes as cationic partners for extended polyiodide arrays, we saw in the structural flexibility offered by the Ag(I) complexes of [9]aneS_3, [15]aneS_5, and [18]aneS_6 a useful attribute in a templating agent for polyiodide anions.



[9]aneS_3



[15]aneS_5



[18]aneS_6

The most common literature procedure for polyiodide synthesis involves the addition of I_2 to the iodide or triiodide of the cation in a single phase.[1,17,18,25] A two-phase synthetic route has also been employed in which an aqueous solution of KI and the complex cation is in contact with a CH_2Cl_2 solution of I_2.[19] Our best results[29−31] have instead been achieved by reacting an excess of I_2 with the PF_6^- or BF_4^- salt of the complex cation in a single phase, the preferred polyiodide being formed via self-assembly.[37]

Thus, reaction of $[Ag([15]aneS_5)](BF_4)$ (prepared in situ from [15]aneS_5 and $AgBF_4$) with 3 molar equiv of I_2 in MeCN, followed by slow evaporation of the solvent, affords dark-red plates after a few days. A single-crystal X-ray structure determination showed that the asymmetric unit consists of two independent $[Ag([15]aneS_5)]^+$ cations anchored to a discrete

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(18) Tebbe, K.-F.; Gilles, T. *Z. Anorg. Allg. Chem.* **1996**, *622*, 138.

(19) Menon, S.; Rajasekharan, M. V. *Inorg. Chem.* **1997**, *36*, 4983.

(20) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1990**, *112*, 1860.

(21) Herbstein, F. H.; Kapon, M. *J. Chem. Soc., Chem. Commun.* **1975**, 677.

(22) Bigoli, F.; Pellinghelli, M. A.; Crisponi, G.; Deplano, P.; Trogu, E. F. *J. Chem. Soc., Dalton Trans.* **1985**, 1349.

(23) Bigoli, F.; Deplano, P.; Devillanova, F. A.; Lippolis, V.; Mercuri, M. L.; Pellinghelli, M. A.; Trogu, E. F. *Inorg. Chim. Acta* **1998**, *267*, 115.

(24) Tebbe, K.-F.; Farida, T. *Z. Naturforsch., Teil B* **1995**, *50*, 1440.

(25) Tebbe, K.-F.; Buchem, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1345.

(26) (a) Tebbe, K.-F. *Acta Crystallogr.* **1983**, *C39*, 154. (b) Crump, W.; Tebbe, K.-F. *Z. Kristallogr. Suppl.* **1991**, *3*, 44.

(27) Deplano, P.; Devillanova, F. A.; Ferraro, J. R.; Mercuri, M. L.; Lippolis, V.; Trogu, E. F. *Appl. Spectrosc.* **1994**, *48*, 1236 and references therein.

(28) (a) Tebbe, K.-F.; Farida, T. *Z. Naturforsch., Teil B* **1995**, *50*, 1685. (b) Tebbe, K.-F.; Bittner, M. *Z. Anorg. Allg. Chem.* **1995**, *621*, 218. (c) Stegemann, H.; Oprea, A.; Nagel, K.; Tebbe, K.-F. *Z. Anorg. Allg. Chem.* **1997**, *623*, 89.

(29) Blake, A. J.; Gould, R. O.; Parsons, S.; Radek, C.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2374.

(30) Blake, A. J.; Lippolis, V.; Parsons, S.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1996**, 2207.

(31) Blake, A. J.; Gould, R. O.; Li, W.-S.; Lippolis, V.; Parsons, S.; Radek, C.; Schröder, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 293.

(32) For examples of I_2 charge-transfer adducts with metal-free thioether crowns see: (a) Blake, A. J.; Cristiani, F.; Devillanova, F. A.; Garau, A.; Gilby, L. M.; Gould, R. O.; Isaia, F.; Lippolis, V.; Parsons, S.; Radek, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1997**, 1337. (b) Blake, A. J.; Li, W.-S.; Lippolis, V.; Schröder, M. *Acta Crystallogr., Sect C* **1997**, *C53*, 886. (c) Blake, A. J.; Cristiani, F.; Devillanova, F. A.; Garau, A.; Gilby, L. M.; Gould, R. O.; Isaia, F.; Lippolis, V.; Parsons, S.; Radek, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1998**, 2037.

(33) (a) Clarkson, J.; Yagbasan, R.; Blower, P. J.; Rawle, S. C.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1987**, 950. (b) Blower, P. J.; Clarkson, J. A.; Rawle, S. C.; Hartman, J. R.; Wolf, R. E.; Yagbasan, R., Jr.; Bott, S. G.; Cooper, S. R. *Inorg. Chem.* **1989**, *28*, 4040.

(34) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. M.; Schröder, M. *Polyhedron* **1989**, *8*, 513.

(35) Küppers, H.-J.; Wieghardt, K.; Tsay, Y.-H.; Krüger, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 575.

(36) Blake, A. J.; Collison, D.; Gould, R. O.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1993**, 521.

(37) Although this synthetic procedure has already been used either with metal complexes or with donor molecules containing sulfur or selenium atoms,[4,12,20,22] a reaction equation has never been proposed, as the identity of the species responsible for the reduction of the diiodine could not always be established. In some cases the oxidation of the donor molecule and/or solvent has been observed [(a) Cristiani, F.; Devillanova, F. A.; Isaia, F.; Verani, G.; Battaglia, L. P.; Bonamartini, A. *J. Chem. Res., Synop.* **1989**, 32. (b) Demartin, F.; Devillanova, F. A.; Isaia, F.; Lippolis, V.; Verani, G. *Inorg. Chim. Acta* **1997**, *255*, 203]. In other cases heterolytic breaking of the I−I bond seems to occur, with the resulting I^+ ion being stabilized by ligand molecules.[4] The formation of I^+ from diiodine by heterolytic breaking of the I−I bond, although not always established, might be the first step toward the formation of polyiodides, especially in MeCN, where this cation can be stabilized [(c) Hua, W. S.; Ajiboye, S. I.; Haining, G.; McGhee, L.; Peacock, R. D.; Peattie, G.; Siddique, R. M.; Winfield, J. M. *J Chem. Soc., Dalton Trans.* **1995**, 3837].

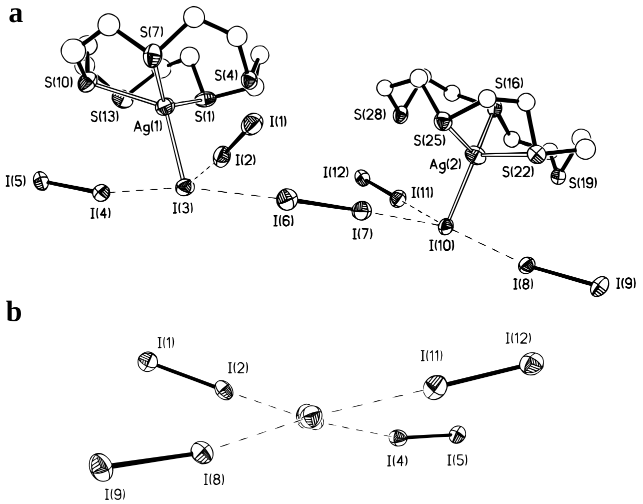

Figure 1. (a) View of the asymmetric unit in $[Ag_2([15]aneS_5)_2]I_{12}$ with the numbering scheme adopted; hydrogen atoms have been omitted for clarity. (b) View of the I_{12}^{2-} polyiodide along the $I^-\cdots I_2\cdots I^-$ fragment direction. Displacement ellipsoids are drawn at 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[Ag_2([15]aneS_5)_2]I_{12}$

Ag(1)−S(1)	2.593(6)	Ag(2)−S(16)	2.614(6)
Ag(1)−S(7)	2.647(6)	Ag(2)−S(22)	2.783(6)
Ag(1)−S(10)	2.724(6)	Ag(2)−S(25)	2.717(6)
Ag(1)−I(3)	2.830(3)	Ag(2)−I(10)	2.781(3)
I(1)−I(2)	2.760(2)	I(3)···I(2)	3.242(2)
I(4)−I(5)	2.770(2)	I(3)···I(4)	3.563(2)
I(6)−I(7)	2.768(2)	I(3)···I(6)	3.517(2)
I(8)−I(9)	2.756(2)	I(10)···I(7)	3.354(2)
I(11)−I(12)	2.755(2)	I(10)···I(8)	3.410(2)
		I(10)···I(11)	3.438(2)
I(1)···S(10^{ii})[a]	3.498(6)		
I(9)···S(4^{i})	3.056(6)		
I(12)···S(19^{iii})	3.131(6)		
I(5)···S(28^{iv})	2.987(6)		
S(1)−Ag(1)−S(7)	132.2(2)	S(16)−Ag(2)−S(22)	107.5(2)
S(1)−Ag(1)−S(10)	109.2(2)	S(16)−Ag(2)−S(25)	115.3(2)
S(7)−Ag(1)−S(10)	79.5(2)	S(22)−Ag(2)−S(25)	73.4(2)
S(1)−Ag(1)−I(3)	102.4(2)	S(16)−Ag(2)−I(10)	120.14(14)
S(7)−Ag(1)−I(3)	111.8(2)	S(22)−Ag(2)−I(10)	116.5(2)
S(10)−Ag(1)−I(3)	122.7(2)	S(25)−Ag(2)−I(10)	114.8(2)
I(7)−I(10)−I(8)	120.58(6)	I(2)−I(3)−I(4)	146.63(6)
I(8)−I(10)−I(11)	153.95(6)	I(4)−I(3)−I(6)	128.05(6)
I(7)−I(10)−I(11)	85.37(5)	I(2)−I(3)−I(6)	84.37(5)

[a] i = $-{}^1/_2 - x, y - {}^1/_2, z - {}^1/_2$; ii = $x - {}^1/_2, {}^1/_2 - y, z$; iii = ${}^1/_2 - x, y - {}^1/_2, z + {}^1/_2$; iv = $1 - x, 1 - y, z - {}^1/_2$.

I_{12}^{2-} polyiodide anion by Ag−I bond interactions; the two complex cations are located on the same side of the polyiodide anion (Figure 1, Table 1). The Ag(I) ions are four coordinate with a very distorted tetrahedral geometry. Three of the five potential S-donor atoms of the macrocyclic ligand are coordinated to each Ag(I) ion [Ag−S, 2.593(6)−2.783(6) Å], with the fourth coordination site occupied by an I^- ion [Ag(2)−I(10), 2.781(3); Ag(1)−I(3), 2.830(3) Å]. The I_{12}^{2-} polyiodide anion can be described as an almost linear I_4^{2-} unit interacting at each of its termini with two diiodine molecules to give an overall twisted "H" configuration; the dihedral angle between the planes containing the two peripheral $I_2\cdots I^-\cdots I_2$ fragments is ca. 40.3° (Figure 1b). The I_4^{2-} unit is formed by one diiodine molecule interacting with two I^-, and consequently the overall I_{12}^{2-} polyiodide is best described as a charge-transfer adduct $[2I^-\cdot 5I_2]$. The I−I bond distances in the I_2 molecules [2.755(2)−2.770(2) Å] are longer than that in I_2 in the vapor [2.667(2) Å][38] or in the solid state [2.715(6) Å].[39] This elongation is attributable to $I^-\cdots I{-}I$ contacts ranging from 3.242(2) to 3.563(2) Å which involve the donation of electron density from I^- to the σ^*-antibonding LUMO of the I_2 molecules.[40,32c] I_{12}^{2-} polyiodides are rare, the only examples being $[K(Crypt\text{-}2.2.2)]_2I_{12}$,[17] $(Me_2Ph_2N)_2I_{12}$,[18] $(MePh_3P)_4I_{22}$,[24] and $[Cu(dafone)_3]I_{12}$ (dafone = 4,5-diazafluoren-9-one).[19] In these compounds the I_{12}^{2-} units are crystallographically centrosymmetric, and for the former three they consist, according to Tebbe et al.,[17,18,24] of two V-shaped I_5^- anions bridged by an I_2 molecule, the angle subtended by the planes containing the I_5^- ions and the bridging I_2 bond axis being ca. 90°. In $(MePh_3P)_4I_{22}$ two further pentaiodide fragments interact "end on" to the I_{12}^{2-} ion to give rise to an overall discrete I_{22}^{4-} ion. In $[Cu(dafone)_3]I_{12}$, although the I_{12}^{2-} anion can still be considered an adduct of the type $[2I^-\cdot 5I_2]$, all of the I atoms are confined to a plane. The structural arrangement is very similar for the I_{12}^{2-} anion in the present case except for the twisting angle between the planes containing the two peripheral $I_2\cdots I^-\cdots I_2$ units (Figure 1b). Presumably, the bulky $[Ag([15]aneS_5)]^+$ cations do not allow the two peripheral $I^-\cdot 2I_2$ fragments in I_{12}^{2-} either to set themselves perpendicular to the bond direction of the central I_2 molecule or to be exactly coplanar with it. In $[Ag_2([15]aneS_5)_2]I_{12}$, an extended three-dimensional superstructure is built up via a network of additional I···S interactions. The terminal iodine atoms [I(1), I(5), I(9), and I(12) in Figure 2] of each terminal I_2 unit in the I_{12}^{2-} ion interact with one S-donor atom of four adjacent $[Ag([15]aneS_5)]^+$ cations. Three of these interactions [I(5)···S(28^{iv}), 2.987(6) Å; I(9)···S(4^{i}), 3.056(6) Å; I(12)···S(19^{iii}), 3.131(6) Å; i = $-{}^1/_2 - x, y - {}^1/_2, z - {}^1/_2$; iii = ${}^1/_2 - x, y - {}^1/_2, z + {}^1/_2$; iv = $1 - x, 1 - y, z - {}^1/_2$] involve sulfur atoms uncoordinated to Ag(I), whereas the fourth involves a sulfur atom already bound to the metal ion [I(1)···S(10^{ii}), 3.498(6) Å; ii = $x - {}^1/_2, {}^1/_2 - y, z$]. These I···S interactions result in a three-dimensional structure composed of spirals of I_{12}^{2-} and $[Ag([15]aneS_5)]^+$ ions alternating along the (001)

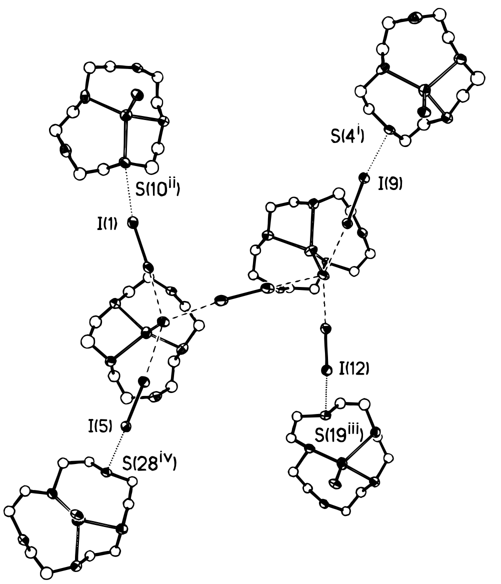

Figure 2. View of $[Ag_2([15]aneS_5)_2]I_{12}$. Dotted lines indicate I···S interactions. Symmetry codes are defined in the footnote to Table 1. Displacement ellipsoids are drawn at 50% probability.

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(38) Karle, I. L. *J. Chem. Phys.* **1955**, *23*, 1739.

(39) van Bolhuis, F.; Koster, P. B.; Migchelsen, T. *Acta Crystallogr.* **1967**, *23*, 90.

(40) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, 1977.

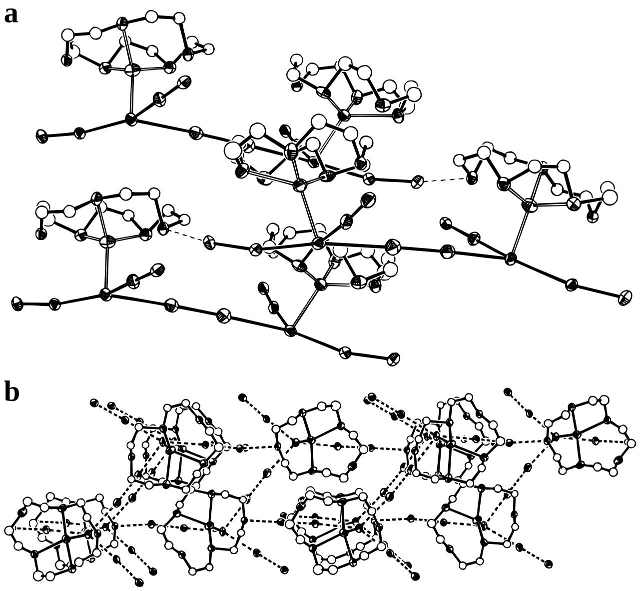

Figure 3. (a) View of $[Ag_2([15]aneS_5)_2]I_{12}$. I_{12}^{2-} anions and $[Ag_2([15]aneS_5)_2]^+$ cations alternate along the *c* axis to form spirals. (b) Projection onto the (110) plane with the iodine atoms joined by thick dashed lines for clarity. Displacement ellipsoids are drawn at 50% probability.

direction (Figure 3a) with a distorted square projection in the (110) plane (Figure 3b).

Since the shape of the complex cation is one of the major parameters which can be manipulated in order to control the self-assembly of the polyiodide anions, we also investigated the cations $[Ag([18]aneS_6)]^+$ and $[Ag([9]aneS_3)_2]^+$ as potential templates. These cations carry the same charge as $[Ag([15]aneS_5)]^+$, but their shape is very different, with $[Ag([18]aneS_6)]^+$ and $[Ag([9]aneS_3)_2]^+$ being essentially spherical. Furthermore, these Ag(I) cations are octahedral and therefore coordinatively saturated with no coordination sites available for I^- ions.

Reaction of $[Ag([18]aneS_6)]BF_4$ (prepared in situ by reaction of $AgBF_4$ with $[18]aneS_6$) with 3 molar equiv of I_2 in $CHCl_3$/$MeNO_2$ (8:5 v/v) affords, after the evaporation of the solvent in vacuo, a dark blue powder. Recrystallizations from MeCN and EtOH give deep-red crystals of $[Ag([18]aneS_6)]I_7$ and brown crystals of $[Ag([18]aneS_6)]I_3$, respectively. The same reaction has been carried out in MeCN using $[Ag([9]aneS_3)_2]BF_4$, and the compound $[Ag([9]aneS_3)_2]I_5$ has been isolated by slow evaporation of the solvent and structurally characterized. The single-crystal structure of $[Ag([18]aneS_6)]I_7$[29] shows the $[Ag([18]aneS_6)]^+$ cations embedded in a three-dimensional polymeric polyiodide matrix of I_7^- anions (Figure 4, Table 2). The overall structure of the $[I_7^-]_\infty$ polyiodide network in the crystal lattice can best be described as a distorted cube in which I^- ions occupy the lattice points of a primitive rhombohedral lattice with one slightly elongated I_2 molecule [I−I, 2.7519(14) Å] placed along each cell edge, bridging two I^- ions [$I^-\cdots I_2$, 3.3564(15) Å]. Each cube edge in this unique three-dimensional network (Figure 5a) consists therefore of an $I^-\cdots I-I\cdots I^-$ arrangement, with each I^- at the cube corners interacting with six I_2 molecules with a local D_{3d} symmetry (Figure 5b). This represents the first example of a "pseudo-octahedral" arrangement of six I_2 molecules around a central I^- anion, in a fashion that resembles the interactions of six ligands with a transition metal to give an octahedral complex. This structure is reminiscent of the perovskite structure observed for $CaTiO_3$: thus, the midpoints of the diiodine molecules replace the positions of O^{2-}, $[Ag([18]aneS_6)]^+$ replaces the central Ca(II) ion, and I^- ions are located at positions normally occupied by Ti(IV).

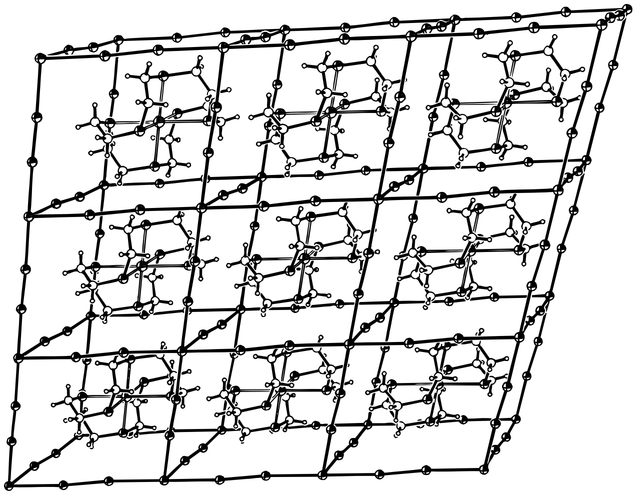

Figure 4. View of the polyiodide matrix in $[Ag([18]aneS_6)]I_7$. Displacement ellipsoids are drawn at 50% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Ag([18]aneS_6)]I_7$

Ag−S(1)	2.754(2)
I(1)···I(2)	3.3564(15)
I(2)−I(2^{i})[a]	2.7519(14)
S(1)−Ag−S(1^{ii})	78.76(4)
S(1^{ii})−Ag−S(1^{iii})	101.24(4)
S(1)−Ag−S(1^{ix})	180.0
I(1)−I(2)−I(2^{i})	175.38(2)
I(2)−I(1)−I(2^{iv})	77.81(2)
I(2)−I(1)−I(2^{vi})	180.0
I(2)−I(1)−I(2^{v})	102.19(2)
I(2^{vii})−I(1)−I(2^{viii})	77.81(2)

[a] i = $-x, -y + 1, -z$; ii = $-y + 1, -x + 1, -z + 1$; iii = $-x + 1, -z + 1, -y + 1$; iv = $-y, -z, -x$; v = z, y, x; vi = $-x, -y, -z$; vii = $-z, -x, -y$; viii = y, z, x; ix = $-x + 1, -y + 1, -z + 1$.

None of the previously reported I_7^- polyiodide species exhibit comparable structure. $[NEt_4]I_7$[8a] and $[(py)_2I]I_7$[8b] exist as two-dimensional networks of symmetrical I_3^- anions linked by I_2 molecules giving the formulation $[I_3^-\cdot(I_2)_2]$ for the heptaiodide unit. The same formulation can be proposed for the discrete I_7^- ion in $[PPh_4]I_7$[3] whereas an adduct of the type $[I_5^-\cdot I_2]$ would be a better description for the polyiodide in bipy·HI_7.[28b] Only four examples are known of I_7^- ions having a trigonal pyramidal geometry and representable as $[I^-\cdot(I_2)_3]$ adducts, namely, $(Hpy)_2I_7I_3$,[26] $[Cu(OETTP)]I_7$,[5] $[(H_3O^+\cdot18\text{-crown-}6)]I_7$,[6] and $[(N\text{-methylbenzothiazole-}2(3H)\text{-thione})_2I]I_7$.[4] In the first three of these, one of the three $I^-\cdots I_2$ interactions is either much longer or much shorter than the other two with I···I distances in the range 3.154(9)−3.354(3) Å. Approximate C_s symmetry can therefore be proposed for the I_7^- ion in these species. In $[(N\text{-methylbenzothiazole-}2(3H)\text{-thione})_2I]I_7$, however, the three I−I distances and the three $I^-\cdots I_2$ interactions lie in the ranges 2.746(1)−2.771(1) and 3.237(1)−3.260(1) Å, respectively, so that an approximate C_{3v} symmetry can be envisaged for the I_7^- ion formulated as an $[I^-\cdot(I_2)_3]$ adduct. The I_7^- anions in $(Hpy)_2I_7I_3$ and $[(H_3O^+\cdot18\text{-crown-}6)]I_7$, like that in $[(N\text{-methylbenzothiazole-}2(3H)\text{-thione})_2I]I_7$, are characterized by head-to-tail long-range interactions [3.426(3)−3.545(13) Å] of the I^- of one I_7^- unit with an I_2 molecule of the next to give infinite one-dimensional chains.

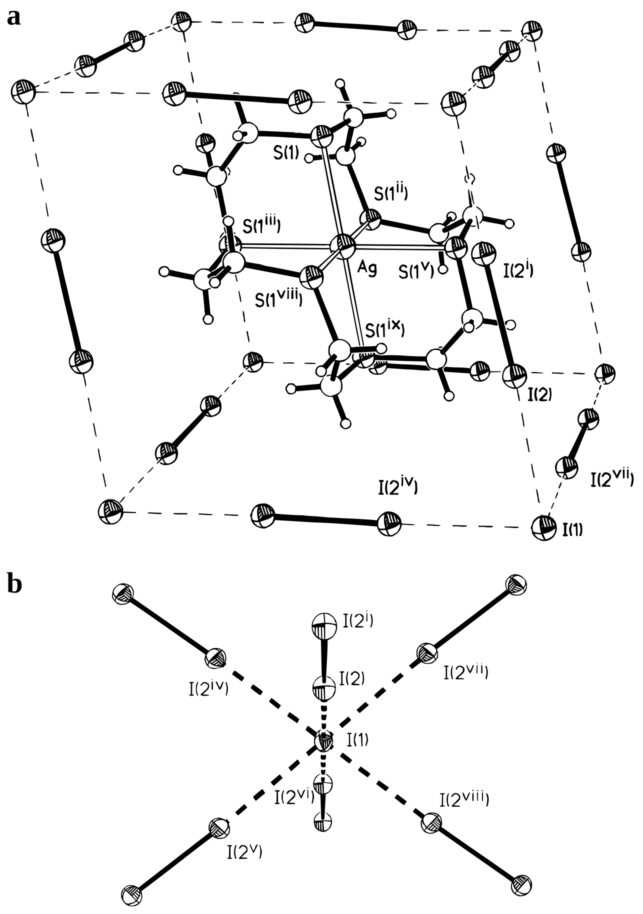

Figure 5. (a) View of the cubelike polyiodide array around the $[Ag([18]aneS_6)]^+$ cation with the numbering scheme adopted. Symmetry codes are defined in the footnote to Table 2. (b) View of an I^- ion interacting with six diiodine molecules with a local D_{3d} symmetry in $[Ag([18]aneS_6)]I_7$. Displacement ellipsoids are drawn at 50% probability.

The template effect of the $[Ag([18]aneS_6)]^+$ cation on the cubic $[I_7^-]_\infty$ structure may be rationalized by comparing the diagonals of the cube of iodines with the spacing of the S_3 triangles making up the faces of the distorted coordination octahedron around Ag(I). The diagonal along the 3-fold axis of the cation is 11.850 Å, while the other diagonals are 17.635 Å. The thickness of the cation may be estimated as the separation of the S_3 triangles (2.48 Å) plus twice the van der Waals radius of the sulfur (1.85 Å), giving 6.18 Å. Its mean diameter may be considered as twice the mean distance of the carbon atoms from the 3-fold axis (3.55 Å) plus twice the van der Waals radius of carbon (1.50 Å), giving 10.10 Å. Therefore the $[Ag([18]aneS_6)]^+$ cations fit very well into the cubic second-sphere framework formed by the I_7^- anions. Conceptually, therefore, the formation of the cubelike $[I_7^-]_\infty$ matrix may be regarded as a second-sphere template reaction around complex cation centers.

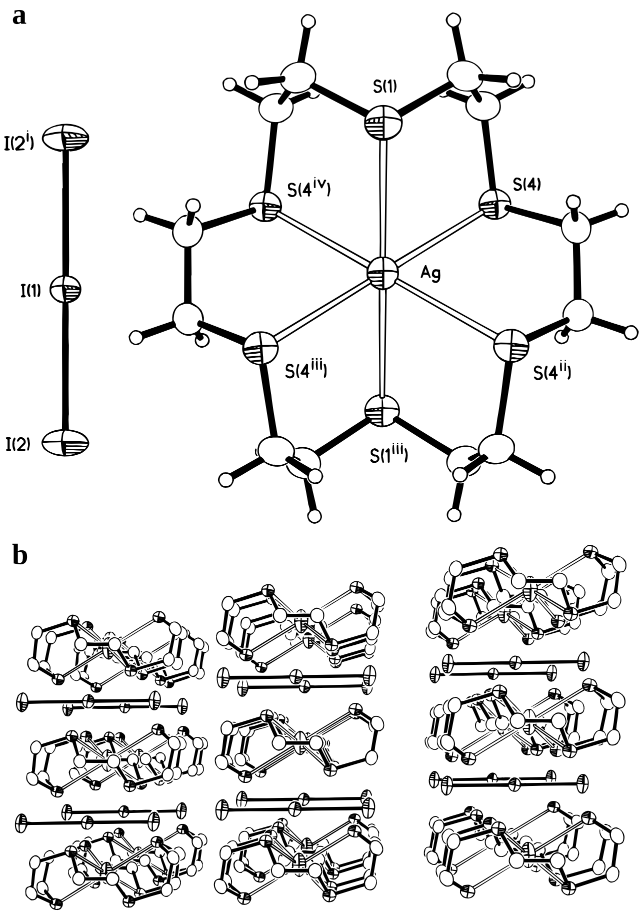

Figure 6. (a) View of $[Ag([18]aneS_6)]I_3$ with the numbering scheme adopted. Symmetry codes are defined in the footnote to Table 3. (b) View of the crystal packing along the *b* axis in $[Ag([18]aneS_6)]I_3$. Displacement ellipsoids are drawn at 50% probability.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Ag([18]aneS_6)]I_3$

Ag−S(1)	2.8007(10)
Ag−S(4)	2.7255(7)
I(1)−I(2)	2.9137(3)
S(1)−Ag−S(4)	78.40(2)
S(1)−Ag−S(1^{iii})^a	180.0
S(1)−Ag−S(4^{ii})	101.60(2)
S(4)−Ag−S(4^{iv})	99.68(3)
S(4)−Ag−S(4^{ii})	80.32(3)
I(2)−I(1)−I(2^{i})	180.0

[a] i = −*x*, −*y*, −*z*; ii = −*x*, *y*, −*z* + 1; iii = −*x*, −*y* + 1, −*z* + 1; iv = *x*, −*y* + 1, *z*.

In contrast, the X-ray crystal structure of $[Ag([18]aneS_6)]I_3$ (Figure 6, Table 3) shows discrete $[Ag([18]aneS_6)]^+$ cations and symmetrical I_3^- ions [I(1)−I(2), 2.9137(3) Å] in the crystal lattice. The packing diagram (Figure 6b) shows a columnar stacking arrangement with parallel stacks of macrocycle complexes and I_3^- ions. This I_3^- salt may be considered a structural precursor to $[Ag([18]aneS_6)]I_7$, to which it may be converted by the addition of 2 equiv of I_2. So far, we have been unable to crystallize the corresponding I_5^- salt which can be regarded as the intermediate between these two structures. It is important to note the different structural modifications of the $[Ag([18]aneS_6)]^+$ cation observed in $[Ag([18]aneS_6)]PF_6$,[34] $[Ag([18]aneS_6)]I_7$, and $[Ag([18]aneS_6)]I_3$. In all three cases the macrocyclic cation adopts a trigonally compressed octahedral geometry with S−Ag−S chelate angles of about 80° and nonchelate angles of about 100°. However, in the I_7^- salt all of the Ag−S distances [2.754(2) Å] are equivalent by symmetry, while the PF_6^- salt shows a tetragonal compression [$Ag-S_{ax}$, 2.697(5) Å; $Ag-S_{eq}$, 2.753(4) Å][34] and the I_3^- salt a tetragonal elongation [Ag−S(1), 2.8007(10) Å; Ag−S(4), 2.7255(7) Å]. The cation is therefore able to adopt somewhat different geometries, which might exert slightly different templating effects during the formation of the polyiodide networks.

Although the $[Ag([9]aneS_3)_2]^+$ cation has potentially the same shape, dimensions, and charge as $[Ag([18]aneS_6)]^+$, it does not show the same template effect: under the same reaction

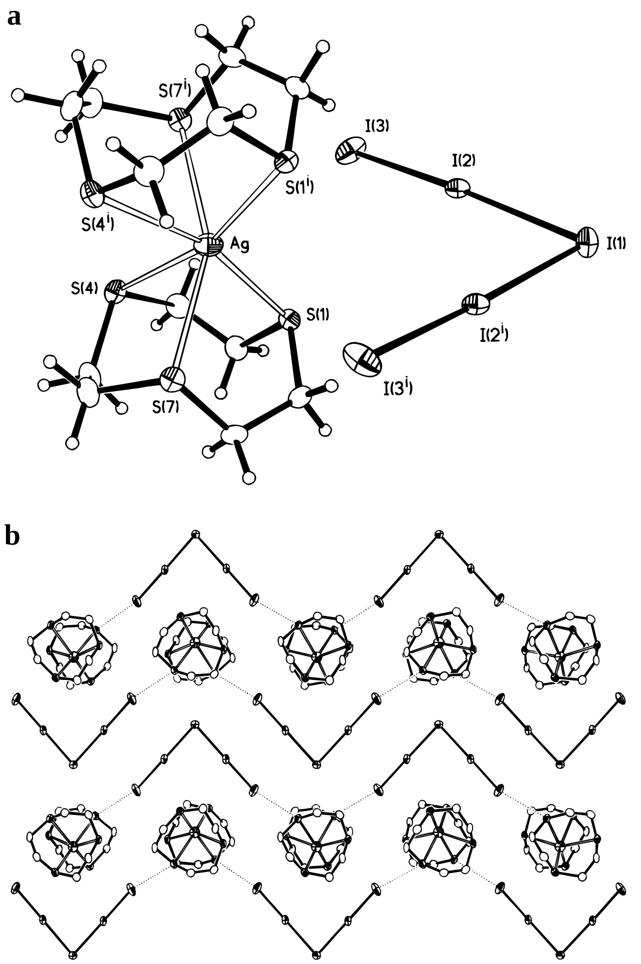

Figure 7. (a) View of $[Ag([9]aneS_5)_2]I_5$ with the numbering scheme adopted; displacement ellipsoids are drawn at 50% probability. Symmetry codes are defined in the footnote to Table 4. (b) Crystal packing in $[Ag([9]aneS_5)_2]I_5$: adjacent chains are related through inversion centers and may be regarded as being in phase with each other but with the cations and anions interchanged. Hydrogen atoms have been omitted for clarity, and displacement ellipsoids are drawn at 70% probability.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Ag([9]aneS_3)_2]I_5$

Ag−S(1)	2.603(2)
Ag−S(4)	2.773(2)
Ag−S(7)	2.777(2)
I(1)−I(2)	3.1118(9)
I(2)−I(3)	2.7898(9)
S(1)−Ag−S(1^i)^a	109.45(7)
S(4)−Ag−S(1^i)	164.01(4)
S(1)−Ag−S(4)	81.68(4)
S(4)−Ag−S(4^i)	90.03(7)
S(1)−Ag−S(7^i)	113.72(6)
S(4)−Ag−S(7^i)	83.58(5)
S(7)−Ag−S(1^i)	113.72(2)
S(1)−Ag−S(7)	81.40(5)
S(4)−Ag−S(7)	78.61(5)
S(7)−Ag−S(7^i)	154.72(7)
I(2)−I(1)−I(2^i)	84.61(4)
I(3)−I(2)−I(1)	177.31(2)

[a] $i = -x, y, -z + {}^1/_2$.

conditions used for the synthesis of $[Ag([18]aneS_6)]I_7$ it forms an I_5^- salt rather than a cubelike $[I_7^-]_\infty$ polyiodide array. A crystal structure determination showed (Figure 7, Table 4) $[Ag([9]aneS_3)_2]^+$ cations and discrete “V”-shaped pentaiodide units (Figure 7a). The cation has structural features very similar to those already reported for other salts,[33,35] with the two molecules of $[9]aneS_3$ bound facially to the Ag(I) metal center, conferring a distorted octahedral arrangement of six sulfur atoms [Ag−S, 2.603(2)−2.777(2) Å]. Each I_5^- unit is best described as an $[I^-{\cdot}(I_2)_2]$ adduct of C_{2v} symmetry [I(1)···I(2), 3.1118(9) Å; I(2)−I(3), 2.7898(9) Å; I(2)−I(1)−I(2^i), 84.61(4)°, $i = -x, y, -z + {}^1/_2$] which is located on a plane perpendicular to the approximate 3-fold axis of the cation. The terminal atoms of each I_5^- unit interact weakly with one sulfur atom in each of two adjacent cations [I···S, 3.618(2) Å] so that a sinusoidal polymeric succession of cations and I_5^- ions develops along the (110) direction (Figure 7b). Each chain alternates with its inversion mate such that the chains pack efficiently. The chains themselves may be regarded as being in phase even though their constituent anions and cations have been interchanged.

FT-Raman Spectroscopy. The structural features of the reported polyiodides are consistent with their FT-Raman spectra. The very strong, broad band at 172 cm^{-1} observed for $[Ag_2([15]aneS_5)_2]I_{12}$ is in agreement with the $[2I^-{\cdot}5I_2]$ adduct formulation for the I_{12}^{2-} polyiodide, in that the simultaneous interaction of the I^- ions with three different I_2 molecules lengthens the I−I distances from 2.715(6) Å in solid I_2[39] to 2.755(2)−2.770(2) Å in the I_{12}^{2-} polyiodide. These slight elongations are indicative of I_2 adducts of medium to weak strength,[41] and one may expect the FT-Raman bands to be shifted to slightly lower frequencies relative to the value of 180 cm^{-1} for I_2 in the solid state.[42] The broadness of the observed band indicates that the absorptions due to ν(I−I) stretching vibrations of the five perturbed diiodine molecules fall very close to each other. The FT-Raman spectrum of $[Ag([18]aneS_6)]I_7$, in which each I^- interacts with six I_2 molecules arranged in D_{3d} symmetry, is particularly interesting because all six I_2 molecules have the same I−I bond distance [2.7519(14) Å]: we would therefore expect only one band below 180 cm^{-1}. In fact, two bands are observed at 179 and 165 cm^{-1}. The stretching vibrations of the six individual slightly perturbed I_2 molecules can combine in D_{3d} symmetry to give two Raman-active normal modes of types $A_{1g} + E_g$. The 179 and 165 cm^{-1} bands can therefore be assigned to A_{1g} and E_g modes, respectively. It is important to note that over the range 500−50 cm^{-1} the Raman spectrum of $[Ag([18]aneS_6)]I_7$ is practically identical to that recorded for [(*N*-methylbenzothiazole-2(3*H*)-thione)$_2$I]I$_7$,[4] in which the polyiodide array has a completely different structure and the basic I_7^- unit is best described as an $[I^-{\cdot}3I_2]$ adduct with an approximate C_{3v} symmetry. In the C_{3v} point group the stretching vibrations of the three individual I_2 molecules combine to give Raman-active normal modes of A_1 + E types. The I_5^- ion in $[Ag([9]aneS_3)_2]I_5$, which has C_{2v} symmetry, can be analyzed similarly; the vibrations of the two individual I_2 units combine to give normal modes of the $A_1 + B_2$ types, and two bands are observed in the FT-Raman spectrum at 162 and 151 cm^{-1}. Finally, the single, very strong band at 118 cm^{-1} observed for $[Ag([18]aneS_6)]I_3$ can be attributed to the symmetric stretch of the symmetric I_3^- ion, the asymmetric stretching and the bending modes being Raman inactive.[27]

Conclusions. We have confirmed that metal complex cations based upon thioether crowns can act as effective templates for the aggregation and assembly of new polyiodide networks. The geometrical features of the complex cation are extremely important as subtle changes in its size and shape can have dramatic effects on the structures of the resulting anionic

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(41) Deplano, P.; Devillanova, F. A.; Ferraro, J. R.; Isaia, F.; Lippolis, V.; Mercuri, M. L. *Appl. Spectrosc.* **1992**, *11*, 1625.

(42) Anderson, A.; Su, T. S. *Chem. Phys. Lett.* **1970**, *6*, 611.

Table 5. Crystallographic Data

	$[Ag_2([15]aneS_5)_2]I_{12}$	$[Ag([18]aneS_6)]I_7$	$[Ag([18]aneS_6)]I_3$	$[Ag([9]aneS_3)_2]I_5$
formula	$C_{10}H_{20}AgI_6S_5$	$C_{12}H_{24}AgI_7S_6$	$C_{12}H_{24}AgI_3S_6$	$C_{12}H_{24}AgI_5S_6$
fw	1169.83	1356.84	849.29	1103.4
cryst syst	orthorhombic	trigonal	monoclinic	monoclinic
space group	$Pna2_1$ (No. 33)	$R\bar{3}m$ (No. 166)	$C2/m$ (No. 12)	$C2/c$ (No. 15)
a (Å)	21.688(4)	9.458(4)	18.5767(11)	17.1117(12)
b (Å)	27.748(4)	9.458(4)	11.9188(7)	12.612(2)
c (Å)	8.623(2)	9.458(4)	5.2714(5)	14.016(2)
α (deg)	90	103.79(3)	90	90
β (deg)	90	103.79(3)	95.634(9)	118.65(4)
γ (deg)	90	103.79(3)	90	90
V (Å^3)	5189.2(2)	758.0(6)	1161.5(2)	2654.5(6)
Z	8	1	2	4
T (K)	200	150	280	150
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73	0.710 73
D_{calcd} (g cm^{-3})	2.995	2.972	2.428	2.760
μ(Mo Kα) (mm^{-1})	8.314	8.207	5.389	7.045
R1[a] $[I > 2\sigma(I)]$	0.0517	0.0192	0.0181	0.0368
wR2[b] (all data)	0.1444	0.0390	0.0422	0.0877

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o)^4\}^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = 1/3[\max(F_o^2,0) + 2F_c^2]$.

polyiodide networks. This work suggests that certain aggregates are preferentially formed at the metal complex cation template, confirming that further new anionic networks, not necessarily derived simply from iodine alone, are accessible, and current work is aimed at the investigation of the formation of related networks with iodine and other main group elements.

Experimental Section

All reagents and solvents were purchased from Aldrich and used without any further purification.

$[Ag_2([15]aneS_5)_2]I_{12}$. [15]aneS$_5$ (30 mg, 0.1 mmol) was dissolved in MeCN (2.5 cm^3) and a solution of $AgBF_4$ (19.5 mg, 0.1 mmol) in MeCN (2.5 cm^3) added. The colorless solution was stirred vigorously for 15 min at room temperature, and subsequently a solution of I_2 (76.0 mg, 0.3 mmol) in MeCN (8 cm^3) was added dropwise. The resulting mixture was stirred at room temperature for 10 min and subsequently allowed to stand. After a week, dark red platy crystals were formed (80 mg, 68.4% yield). Elem. anal. Found (calcd for $C_{10}H_{20}AgI_6S_5$): C, 10.52 (10.27); H, 1.55 (1.72). FT-Raman in the range 500−50 cm^{-1} ν(I−I) (relative intensity): 172 (100), 72 (6) cm^{-1}. A crystal having dimensions 0.53 × 0.32 × 0.10 mm was used for diffraction studies.

$[Ag([18]aneS_6)]I_7$ and $[Ag([18]aneS_6)]I_3$. [18]aneS$_6$ (90 mg, 0.25 mmol) was dissolved in $CHCl_3$ (3 cm^3) and a solution of $AgBF_4$ (48.6 mg, 0.25 mmol) in $MeNO_2$ (5 cm^3) added. The solution was stirred at room temperature for 15 min, and subsequently a solution of I_2 (190 mg, 0.75 mmol) in $CHCl_3$ (5 cm^3) was added. The residue obtained after removal of the solvent in vacuo was partially recrystallized from MeCN to give deep red blocks of $[Ag([18]aneS_6)]I_7$ (a crystal having dimensions 0.23 × 0.15 × 0.12 mm was used for diffraction studies). Elem. anal. Found (calcd for $C_{12}H_{24}AgI_7S_6$): C, 11.11(10.62); H, 1.76 (1.78). FT-Raman in the range 500−50 cm^{-1} ν(I−I) (relative intensity): 179 (37), 165 (100) cm^{-1}. Recrystallization of the remaining residue from EtOH afforded brown columnar blocks of $[Ag([18]aneS_6)]I_3$ (a crystal having dimensions 0.38 × 0.16 × 0.16 mm was used for diffraction studies). Elem. anal. Found (calcd for $C_{12}H_{24}AgI_3S_6$): C, 17.34 (16.97); H, 2.77 (2.85). FT-Raman in the range 500−50 cm^{-1} ν(I−I): 118 cm^{-1}.

$[Ag([9]aneS_3)_2]I_5$. A solution of $AgBF_4$ (27.84 mg, 0.143 mmol) in MeCN (4 cm^3) was added to a solution of [9]aneS$_3$ (51.6 mg, 0.286 mmol) in $CHCl_3$/MeCN (2 cm^3 1:1 v:v). The resulting mixture was stirred at room temperature for 30 min. A solution of I_2 (109 mg, 0.429 mmol) in MeCN (10 cm^3) was then added dropwise. The solvent was removed under reduced pressure to give a dark-red residue, which was dissolved in hot MeCN/$MeNO_2$ (5 cm^3 1:1 v:v); dark red blocks were formed from the resulting solution after several days of slow evaporation (77.2 mg, 49% yield). Elem. anal. Found (calcd for $C_{12}H_{24}AgI_5S_6$): C, 12.88 (13.0); H, 2.24 (2.19). FT-Raman in the range 500−50 cm^{-1} ν(I−I) (relative intensity): 162 (100), 151 (100), 106 (20), 95 (20) cm^{-1}. A crystal having dimensions 0.20 × 0.18 × 0.12 mm was used for diffraction studies.

FT-Raman Measurements. FT-Raman spectra (resolution 4 cm^{-1}) were recorded at room temperature on a Bruker RF 100 FTR spectrometer, fitted with an In−Ga−As detector and operating with an excitation frequency of 1064 nm. Power levels of the Nd:YAG laser source varied between 20 and 100 mW. The solid samples were packed into a suitable cell and fitted into the compartment designed for 180° scattering geometry. No decomposition was observed during the experiments. The values in parentheses next to the ν(I−I) values represent the intensities of the peaks relative to the strongest, taken equal to 100.

Crystal Structure Determinations. Details of all four structure determinations appear in Table 5. Only special features of the analyses are noted here. Data collection was performed on a Stoë Stadi-4 four-circle diffractometer for $[Ag_2([15]aneS_5)_2]I_{12}$, $[Ag([18]aneS_6)]I_7$, and $[Ag([18]aneS_6)]I_3$ and on an Enraf-Nonius FAST TV diffractometer for $[Ag([9]aneS_3)_2]I_5$. The temperature was controlled using an Oxford Cryosystem open-flow cryostat.[43]

Crystal Structure of $[Ag_2([15]aneS_5)_2]I_{12}$. A total of 5756 reflections was collected to $2\theta_{max} = 50°$ as $\omega-\theta$ scans using on-line profile-fitting[44] and yielding 5104 unique reflections ($R_{int} = 0.0203$, 4640 with $I > 2\sigma(I)$). Data were corrected for Lorentz and polarization effects and for absorption by means of ψ-scans (maximum and minimum transmission factors 0.1101, 0.0225). The structure was solved by direct methods using SHELXS-86[45] and refined on F^2 (297 parameters) using SHELXL-96.[46] All non-H atoms were refined anisotropically, and H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. The largest features in the final difference map corresponded to 1.80 and −1.94 e Å^{-3} and were located 0.87 and 0.94 Å from I(5) and I(2), respectively.

Crystal Structures of $[Ag([18]aneS_6)]I_7$ and $[Ag([18]aneS_6)]I_3$. Data were acquired as $\omega-2\theta$ scans using on-line profile-fitting.[44] A total of 1332 reflections was collected to $2\theta_{max} = 45°$ for $[Ag([18]aneS_6)]I_7$, yielding 383 unique reflections ($R_{int} = 0.060$, 380 with $I > 2\sigma(I)$); for $[Ag([18]aneS_6)]I_3$, 2740 reflections were acquired to $2\theta_{max} = 50°$, yielding 1074 unique reflections ($R_{int} = 0.0130$, 988 with $I > 2\sigma(I)$). Data were corrected for Lorentz and polarization effects and for absorption by means of ψ-scans (maximum and minimum transmission factors 0.368, 0.299 for $[Ag([18]aneS_6)]I_7$; 0.164, 0.131 for $[Ag([18]aneS_6)]I_3$). A Patterson synthesis (SHELXS-86)[45] was used to

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(43) Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105.

(44) Clegg, W. *Acta Crystallogr.* **1981**, *A37*, 22.

(45) Sheldrick, G. M. *SHELXS-86*, *SHELXS-96*, *Programs for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986−1996.

(46) Sheldrick, G. M. *SHELXL-93*, *SHELXL-96*, *Programs for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993−1996.

locate the iodine and silver atoms in each structure, from which point the structures were developed by iterative cycles of least-squares refinement and difference Fourier synthesis. The structures were refined by full-matrix least squares on F^2 (SHELXL-93)[46] (37 and 58 parameters refined for $[Ag([18]aneS_6)]I_7$ and $[Ag([18]aneS_6)]I_3$, respectively) with anisotropic thermal parameters for all non-H atoms. H atoms were included in fixed calculated positions with $U_{iso}(H) = 1.2U_{eq}(C)$. The largest features in the final ΔF synthesis were lower than 1.07 e Å^{-3} for both of the structures.

Crystal Structure of $[Ag([9]aneS_3)_2]I_5$. The crystal was attached to a glass fiber using grease, and data were acquired on an Enraf-Nonius FAST TV diffractometer using area detector scans.[47] A total of 5379 reflections was collected, yielding 2003 unique reflections ($R_{int} = 0.088$, 1863 with $I > 2\sigma(I)$). The structure was solved by a combination of direct and Fourier methods using SHELXS-96,[45] and refinements were performed on F^2 (111 parameters) using SHELXL-96.[46] All non-H atoms were refined anisotropically, and H atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. The highest peak (1.35 e Å^{-3}, 0.91 Å from I(3)) and the lowest trough (−1.43 e Å^{-3}, 2.37 Å from I(1)) in the final ΔF synthesis possess no chemical significance.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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(47) Darr, J. A.; Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A. *Inorg. Chem.* **1993**, *32*, 5704.