Self-Assembly of Ribbons and Frameworks Containing Large Channels Based upon Methylene-Bridged Dithio-, Diseleno-, and Ditelluroethers

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Homoleptic copper(I) and silver(I) complexes $[M_n(L\text{-}L)_{2n}](BF_4)_n$ (M = Cu or Ag; L-L = $MeECH_2EMe$; E = S, Se or Te) have been prepared and characterized by analysis, FAB mass spectrometry, and IR and multinuclear NMR spectroscopy (^1H, ^{77}Se, ^{125}Te, ^{63}Cu and ^{109}Ag). The single-crystal X-ray structures of $[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$ (orthorhombic, $P2_12_12_1$, $a = 10.879(7)$ Å, $b = 16.073(7)$ Å, $c = 9.19(1)$ Å, $Z = 4$) and $[Ag_n(MeSeCH_2SeMe)_{2n}](BF_4)_n$ (monoclinic, $P2_1/c$, $a = 14.546(9)$ Å, $b = 14.65(1)$ Å, $c = 30.203(9)$ Å, $Z = 4$) reveal extended three-dimensional cationic frameworks in the solid state which contain large cylindrical or rectangular channels accommodating the PF_6^- or BF_4^- counterions. In contrast, a single-crystal X-ray structure of $[Cu_n(MeSCH_2SMe)_{2n}](PF_6)_n\cdot nMeNO_2$ (orthorhombic, $Pbcn$, $a = 15.506(3)$ Å, $b = 8.934(2)$ Å, $c = 25.859(3)$ Å, $Z = 8$) shows tetrahedral Cu(I) ions coordinated to bridging dithioethers forming an cationic ribbon-like arrangement of 8-membered rings. Adjacent rings are linked by the Cu atoms. Variable temperature NMR studies have been used to probe various exchange processes occurring in solution in these systems.

Introduction

The rational construction of extended structures incorporating large cavities or channels capable of hosting small molecules is an area of considerable current interest due to their potential applications in, for example, catalysis or separation procedures. While there are now many examples based upon silica and alumina frameworks and doped-derivatives, ordered networks of this type based upon inorganic coordination compounds are much less common.[1−7] The majority of examples involve copper and silver complexes of nitrogen ligands derived from 4,4'-bipyridyl,[2−4] piperazine,[5] pyrazine,[5,6] or organocyanides,[7] and some of the general procedures are discussed in a recent review by Robson and co-workers.[1] We recently reported the synthesis and structural studies on a series of complexes of silver(I) with potentially bidentate group 16 donor ligands involving di- and trimethylene backbones, $RE(CH_2)_nER$ (E = S, Se or Te; $n = 2, 3$).[8,9] While the complexes with dimethylene backbones are mononuclear with chelated ligands, we were able to show that the corresponding trimethylene backboned ligands yielded unusual polymeric structures. In view of these results we proposed that the methylene-bridged bidentate ligands $MeECH_2EMe$ (E = S, Se, or Te) would disfavor chelation, due to ring strain, and might therefore promote formation of ordered extended arrays involving bridging dithio-, diseleno-, or ditelluroether ligands. Indeed previous work has shown that these ligands adopt only bridging or monodentate bonding modes with for example Pd(II), Pt(II), or Au(I), forming either dinuclear or mononuclear complexes.[10−12] The group 15 analogue of these ligands, dppm ($Ph_2PCH_2PPh_2$), has been extensively studied[13,14] and its chemistry has yielded many interesting structural and chemical features, yet the group 16 ligands studied here have received very little study. A small number of examples of extended structures have been reported previously for Cu(I) and Ag(I) complexes incorporating macrocyclic thioether and selenoether ligands.[15−19] In this paper we report the synthesis of the silver(I) and copper(I) species $[M_n(MeECH_2EMe)_{2n}]^{n+}$, all of which adopt unprecedented structures in the solid state, involving either one-dimensional ribbon-like arrays or three-dimensional networks incorporating large channels which accommodate the PF_6^- or BF_4^- anions. The products have been characterized both in the solid state, through single-crystal X-ray analyses on three examples, and in solution, through the use of multinuclear NMR spectroscopy (^{109}Ag, ^{63}Cu, ^{77}Se, and ^{125}Te). This particular combination of techniques permits a more detailed understanding of the species obtained and their structures in solution and in the solid state. Attempts to characterize corresponding complexes of $PhECH_2EPh$ ligands

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Table 1. Crystallographic Data

	$[Cu_n(MeSCH_2SMe)_{2n}](PF_6)_n{\cdot}nCH_3NO_2$	$[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$	$[Ag_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$
chem formula	$C_7H_{19}CuF_6NO_2PS_4$	$C_6H_{16}CuF_6PSe_4$	$C_{24}H_{64}Ag_4B_4F_{16}Se_{16}$
fw	486.0	612.5	2394.8
T, °C	−123	−123	−123
space group	*Pbcn*	$P2_12_12_1$	$P2_1/c$
a, Å	15.506(3)	10.879(7)	14.546(9)
b, Å	8.934(2)	16.073(7)	14.65(1)
c, Å	25.859(3)	9.19(1)	30.203(9)
β, deg	90	90	100.98(4)
V, Å^3	3582(2)	1607(1)	6318(5)
Z	8	4	4
D_{calcd}, g cm^{-3}	1.802	2.531	2.517
μ(Mo Kα), cm^{-1}	18.32	105.58	105.05
R^a	0.049	0.042	0.061
$R_w{}^b$	0.050	0.046	0.063

[a] $R = \sum(|F_{obs}|_i - |F_{calc}|_i)/\sum|F_{obs}|_i$. [b] $R_w = [\sum w_i(|F_{obs}|_i - |F_{calc}|_i)^2/\sum w_i|F_{obs}|_i{}^2]^{1/2}$

resulted in species with variable analytical compositions, and these studies were not pursued.

Experimental Section

Physical measurements were made as described elsewhere.[9] Silver-109 NMR spectra were recorded on a Bruker AM360 spectrometer at 16.75 MHz. Spectra were obtained from solutions in CH_3NO_2 containing 5% of the deuteriated analogue to provide the lock, in 10 mm o.d. tubes. Spectra were recorded by direct observation from solutions containing the free radical relaxation agent TEMPO (TANOL)[20] and with a 2 s pulse delay, typically 20 000 scans being accumulated. A 9.1 mol dm^{-3} solution of $AgNO_3$ in D_2O containing Fe^{3+} as relaxation agent was used as zero reference.[21] This "zero" is +47 ppm from the Ag^+ resonance at "infinite dilution". Copper-63 NMR were recorded at 95.5MHz also on a Bruker AM360 and referenced to $[Cu(MeCN)_4]^+$ (0 ppm) in MeCN at 300 K.

Synthesis. The following ligands were made by literature methods: $MeSCH_2SMe$,[22] $MeSeCH_2SeMe$,[23] and $MeTeCH_2TeMe$.[24] The complexes were prepared by the same general method described below, with minor modifications in certain cases. Complexes were made under a nitrogen atmosphere, and samples were stored in sealed containers wrapped in aluminium foil in a freezer. Most of the silver complexes are light sensitive to some degree and darken rapidly in solution in diffuse daylight.

Silver Complexes. $[Ag_n(L\text{-}L)_{2n}](BF_4)_n$. The ligand L-L (2 mmol) was added to a suspension of dry powdered $AgBF_4$ (1 mmol) in dichloromethane (10 cm^3). The solution was then decanted from any insoluble material and diethyl ether added to yield a white solid. The solid was filtered off, rinsed with diethyl ether (3 × 10 cm^3) and dried *in vacuo* in the dark. Yields typically 60%. Compounds were recrystallized from $MeNO_2$/diethyl ether where necessary. $[Ag_n(MeSCH_2SMe)_{2n}](BF_4)_n$. Anal. Calcd for $C_6H_8AgBF_4S_4$: C, 17.5; H, 3.9. Found: C, 17.4; H, 4.2. ^{1}H NMR spectrum (90 MHz, CD_3NO_2, 298 K): δ 4.00 (*s*, SCH_2S, 4H), 2.50 (*s*, CH_3S, 12H).

$[Ag_n(MeSeCH_2SeMe)_{2n}](BF_4)_n$. Anal. Calcd for $C_6H_8AgBF_4Se_4$: C, 12.0; H, 2.7. Found: C, 11.8; H, 2.3. ^{1}H NMR spectrum (90 MHz, CD_3NO_2, 298 K): δ 4.05 (*s*, $SeCH_2Se$, 4H), 2.50 (*s*, CH_3Se, 12H).

$[Ag_n(MeTeCH_2TeMe)_{2n}](BF_4)_n$. The ligand (2 mmol) was added to a suspension of dry powdered $AgBF_4$ (1 mmol) in dichloromethane (10 cm^3) yielding an insoluble yellow solid. This solid was filtered off and washed with $MeNO_2$. The washings were then treated with diethyl ether to give a pale yellow solid. Anal. Calcd for $C_6H_8AgBF_4Te_4$: C; 9.1, H; 2.0. Found: C; 9.4, H; 2.1. ^{1}H NMR spectrum (90 MHz, CD_3NO_2, 298 K): δ 3.70 (*s*, $TeCH_2Te$, 4H), 2.35 (*s*, CH_3Te, 12H).

Copper Complexes. $[Cu_n(L\text{-}L)_{2n}](PF_6)_n$. To a solution of $[Cu(MeCN)_4]PF_6$[25] (1 mmol) in CH_2Cl_2 (10cm^3) the ligand was added giving a colorless solution. The solution was then poured into diethyl ether with stirring to give a white solid. The solid was filtered off, rinsed with diethyl ether (3 × 10 cm^3) and dried *in vacuo*. Yields were typically 50−80%. $[Cu_n(MeSCH_2SMe)_{2n}](PF_6)_n$. Anal. Calcd for $C_6H_8CuF_6PS_4$: C; 17.0, H; 3.8. Found: C; 16.8, H; 3.1. ^{1}H NMR spectrum (90 MHz, CD_3NO_2, 298 K): δ 4.10 (*s*, SCH_2S, 4H), 2.55 (*s*, CH_3S, 12H).

$[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$. Anal. Calcd for $C_6H_8CuF_6PSe_4$: C, 11.8; H, 2.6. Found: C, 11.5; H, 2.4. ^{1}H NMR spectrum (90 MHz, CD_3NO_2, 298 K): δ 4.00 (*s*, $SeCH_2Se$, 4H), 2.45 (*s*, CH_3Se, 12H).

$[Cu_n(MeTeCH_2TeMe)_{2n}](PF_6)_n$. Anal. Calcd for $C_6H_8CuF_6PTe_4$: C, 8.9; H, 2.0. Found: C, 8.9; H, 2.0. ^{1}H NMR spectrum (90 MHz, CD_3NO_2, 298 K): δ 3.70 (*s*, $TeCH_2Te$, 4H), 2.30 (*s*, CH_3Te, 12H).

X-ray Crystallography. Details of the crystallographic data are given in Table 1 for the three structures. In each case the selected crystal was coated with mineral oil and mounted on a glass fiber. Data collection used a Rigaku AFC7S four-circle diffractometer equipped with an Oxford Cryostreams low temperature attachment, using graphite-monochromated Mo Kα X-radiation. The intensities of three standard reflections were measured after every 150 data. At convergence the weighting scheme $w^{-1} = \sigma^2(F)$ gave satisfactory agreement analyses in each case.

$[Cu_n(MeSCH_2SMe)_{2n}](PF_6)_n{\cdot}nMeNO_2$. No significant crystal decay or movement was observed. As there were no identifiable faces, the data were corrected for absorption using ψ-scans. The structure was solved by direct methods[26] and developed by using iterative cycles of full-matrix least-squares refinement and difference Fourier syntheses which located all non-H atoms.[27] The cationic $[Cu(MeSCH_2SMe)_2]^+$ repeating unit and two discrete half $PF_6{}^-$ anions in the asymmetric unit were found to be ordered, and during refinement one fully occupied $MeNO_2$ solvent molecule was identified per Cu(I) center. P(1) occupies a crystallographic inversion center at (0.5,0,0.25), with three F-atoms in general positions related by this inversion center. In the other $PF_6{}^-$ anion F(6), P(2), and F(7) are 50% occupied and lie along a crystallographic 2-fold axis, (0.5,y,0.25), with the F(4) and F(5) occupying general positions. The Cu, S, P, and F atoms were refined anisotropically, while H-atoms were included in fixed, calculated positions. The data:parameter ratio did not warrant refining the other non-H atoms anisotropically.

$[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$. No significant crystal decay or movement was observed. As there were no identifiable faces, the data were corrected for absorption using ψ-scans. The structure was solved

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_n(MeSeCH_2SeMe)_{2n}]^{n+}$

Se(1)−Cu(1)	2.460(2)	Se(1)−C(1)	1.93(2)
Se(1)−Cu(1)	1.93(2)	Se(2)−Cu(1)	2.417(3)
Se(2)−C(3)	1.94(2)	Se(2)−C(4)	1.94(2)
Se(3)−Cu(1)	2.442(3)	Se(3)−C(2)	1.98(1)
Se(3)−C(5)	1.96(2)	Se(4)−Cu(1)	2.399(3)
Se(4)−C(4)	1.95(2)	Se(4)−C(6)	1.92(2)
Cu(1)−Se(1)−C(1)	107.9(5)	Cu(1)−Se(1)−C(2)	100.8(4)
C(1)−Se(1)−C(2)	97.9(8)	Cu(1)−Se(2)−C(3)	122.3(6)
Cu(1)−Se(2)−C(4)	102.4(5)	C(3)−Se(2)−C(4)	98.0(7)
Cu(1)−Se(3)−C(2)	99.7(5)	Cu(1)−Se(3)−C(5)	103.2(6)
C(2)−Se(3)−C(5)	96.8(7)	Cu(1)−Se(4)−C(4)	105.0(5)
Cu(1)−Se(4)−C(6)	108.3(7)	C(4)−Se(4)−C(6)	97.7(9)
Se(1)−Cu(1)−Se(2)	103.87(9)	Se(1)−Cu(1)−Se(3)	108.32(9)
Se(1)−Cu(1)−Se(4)	108.3(1)	Se(2)−Cu(1)−Se(3)	111.5(1)
Se(2)−Cu(1)−Se(4)	116.89(10)	Se(3)−Cu(1)−Se(4)	107.65(10)
Se(1)−C(2)−Se(3)	113.9(7)	Se(2)−C(4)−Se(4)	110.8(8)

Table 3. Fractional Atomic Coordinates for $[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$

atom	*x*	*y*	*z*
Se(1)	0.6136(1)	0.50662(6)	0.0753(1)
Se(2)	0.7925(1)	0.68412(6)	−0.1071(1)
Se(3)	0.8593(1)	0.62971(6)	0.3118(1)
Se(4)	0.5439(1)	0.73287(1)	0.2177(1)
Cu(1)	0.7027(1)	0.64454(7)	0.1232(1)
P(1)	0.0635(4)	0.4558(2)	0.0317(4)
F(1)	0.008(1)	0.4485(5)	−0.124(1)
F(2)	0.1764(8)	0.4006(5)	−0.007(1)
F(3)	0.144(2)	0.535(1)	−0.040(2)
F(4)	0.134(2)	0.484(1)	0.176(2)
F(5)	−0.037(2)	0.528(1)	0.059(2)
F(6)	−0.005(2)	0.393(1)	0.124(2)
F(7)	−0.010(3)	0.365(2)	0.026(4)
F(8)	0.089(3)	0.417(2)	0.200(4)
F(9)	0.128(2)	0.533(2)	0.070(3)
F(10)	−0.068(2)	0.489(2)	0.095(3)
C(1)	0.446(1)	0.5225(7)	0.011(1)
C(2)	0.6854(9)	0.4816(6)	−0.111(1)
C(3)	0.716(1)	0.7830(7)	−0.189(1)
C(4)	0.947(1)	0.7343(6)	−0.048(1)
C(5)	0.792(1)	0.6945(6)	0.474(1)
C(6)	0.615(1)	0.8397(8)	0.260(2)

by heavy atom Patterson methods[28] and developed by using iterative cycles of full-matrix least-squares refinement and difference Fourier syntheses which located all non-H atoms for the cationic $[Cu(MeSeCH_2SeMe)_2]^+$ repeating unit and discrete PF_6^- anion in the asymmetric unit.[27] During refinement some disorder was identified in the PF_6^- anion. This was modelled successfully by using partial F-atom occupancies for F(3)−F(6). Thus, F(3)−F(6) have occupancies of 0.6, while F(7)−F(10) have occupancies of 0.4. Although F(1) and F(2) have higher than expected thermal parameters, alternative sites could not be clearly identified. All non-H atoms, except for the partially occupied F atoms, were refined anisotropically, while H atoms were included in fixed, calculated positions. The absolute configuration was checked by inverting the structure; the configuration chosen showed smaller esd's on the atomic coordinates and slightly smaller R and R_w values at convergence. The Flack parameter also indicated that the correct configuration had been chosen.[29]

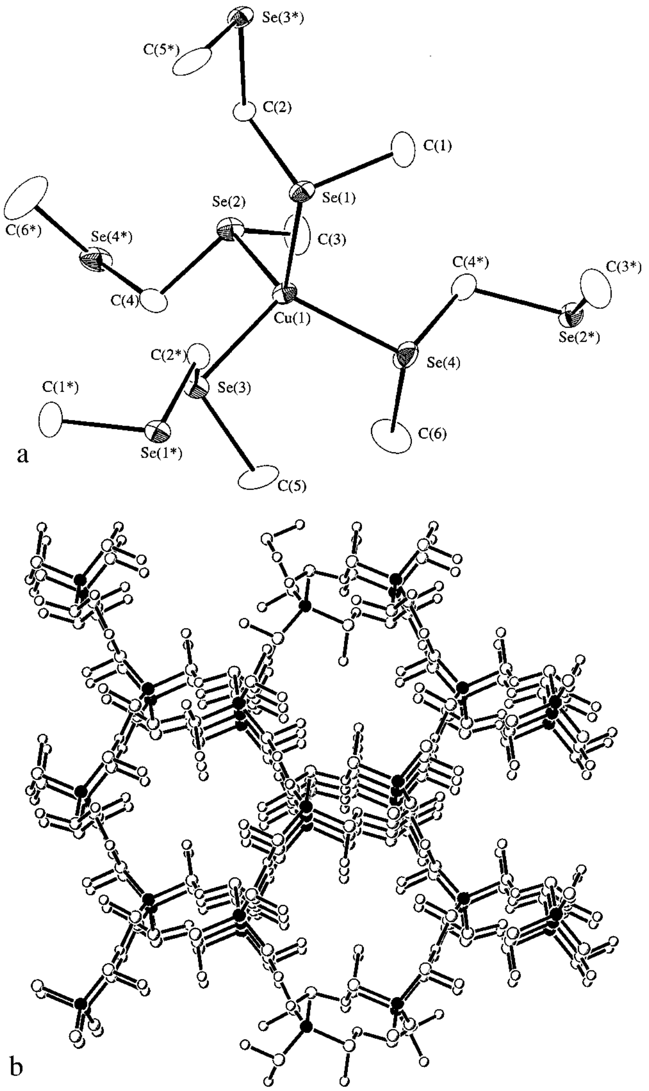

Figure 1. (a) View of mononuclear cation fragment, $[Cu(MeSeCH_2SeMe)_2]^+$, in the asymmetric unit showing the numbering scheme adopted and the nearest symmetry related neighbors (marked by an asterisk). (b) View down the *c*-axis of the polymeric 3-D network formed by $[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$ illustrating the channels formed. Cu atoms are shaded; H-atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and angles (deg) for $[Ag_n(MeSeCH_2SeMe)_{2n}]^{n+}$

Ag(1)−Se(1)	2.676(4)	Ag(1)−Se(2)	2.687(4)
Ag(1)−Se(3)	2.703(4)	Ag(1)−Se(4)	2.688(5)
Ag(2)−Se(5)	2.687(4)	Ag(2)−Se(6)	2.676(4)
Ag(2)−Se(7)	2.704(4)	Ag(2)−Se(8)	2.640(4)
Ag(3)−Se(9)	2.666(4)	Ag(3)−Se(10)	2.706(4)
Ag(3)−Se(11)	2.727(4)	Ag(3)−Se(12)	2.676(4)
Ag(4)−Se(13)	2.679(4)	Ag(4)−Se(14)	2.681(4)
Ag(4)−Se(15)	2.678(4)	Ag(4)−Se(16)	2.687(4)
Se(1)−Ag(1)−Se(2)	118.0(1)	Se(1)−Ag(1)−Se(3)	104.4(1)
Se(1)−Ag(1)−Se(4)	115.9(1)	Se(2)−Ag(1)−Se(3)	112.3(1)
Se(2)−Ag(1)−Se(4)	101.0(1)	Se(3)−Ag(1)−Se(4)	104.8(1)
Se(5)−Ag(2)−Se(6)	116.9(1)	Se(5)−Ag(2)−Se(7)	98.2(1)
Se(5)−Ag(2)−Se(8)	115.7(1)	Se(6)−Ag(2)−Se(7)	101.7(1)
Se(6)−Ag(2)−Se(8)	115.6(2)	Se(7)−Ag(2)−Se(8)	104.9(1)
Se(9)−Ag(3)−Se(10)	109.9(1)	Se(9)−Ag(3)−Se(11)	100.2(4)
Se(9)−Ag(3)−Se(12)	117.7(1)	Se(10)−Ag(3)−Se(11)	107.3(1)
Se(10)−Ag(3)−Se(12)	101.0(1)	Se(11)−Ag(3)−Se(12)	120.3(1)
Se(13)−Ag(4)−Se(14)	101.9(1)	Se(13)−Ag(4)−Se(15)	110.0(1)
Se(13)−Ag(4)−Se(16)	113.7(1)	Se(14)−Ag(4)−Se(15)	111.9(1)
Se(14)−Ag(4)−Se(16)	117.4(1)	Se(15)−Ag(4)−Se(16)	102.2(1)

$[Ag_n(MeSeCH_2SeMe)_{2n}](BF_4)_n$. During data collection the standards showed an 8.7% decay in intensity. A linear decay correction was therefore applied to the data. The structure was solved by direct methods[30] and developed by using iterative cycles of full-matrix least-squares refinement and difference Fourier syntheses which located all non-H atoms for the cationic $[Ag_4(MeSeCH_2SeMe)_8]^{4+}$ repeating unit and four discrete BF_4^- anions in the asymmetric unit.[27] During refinement some disorder was identified in one of the BF_4^- anions. This was modelled successfully by using partial F-atom occupancies

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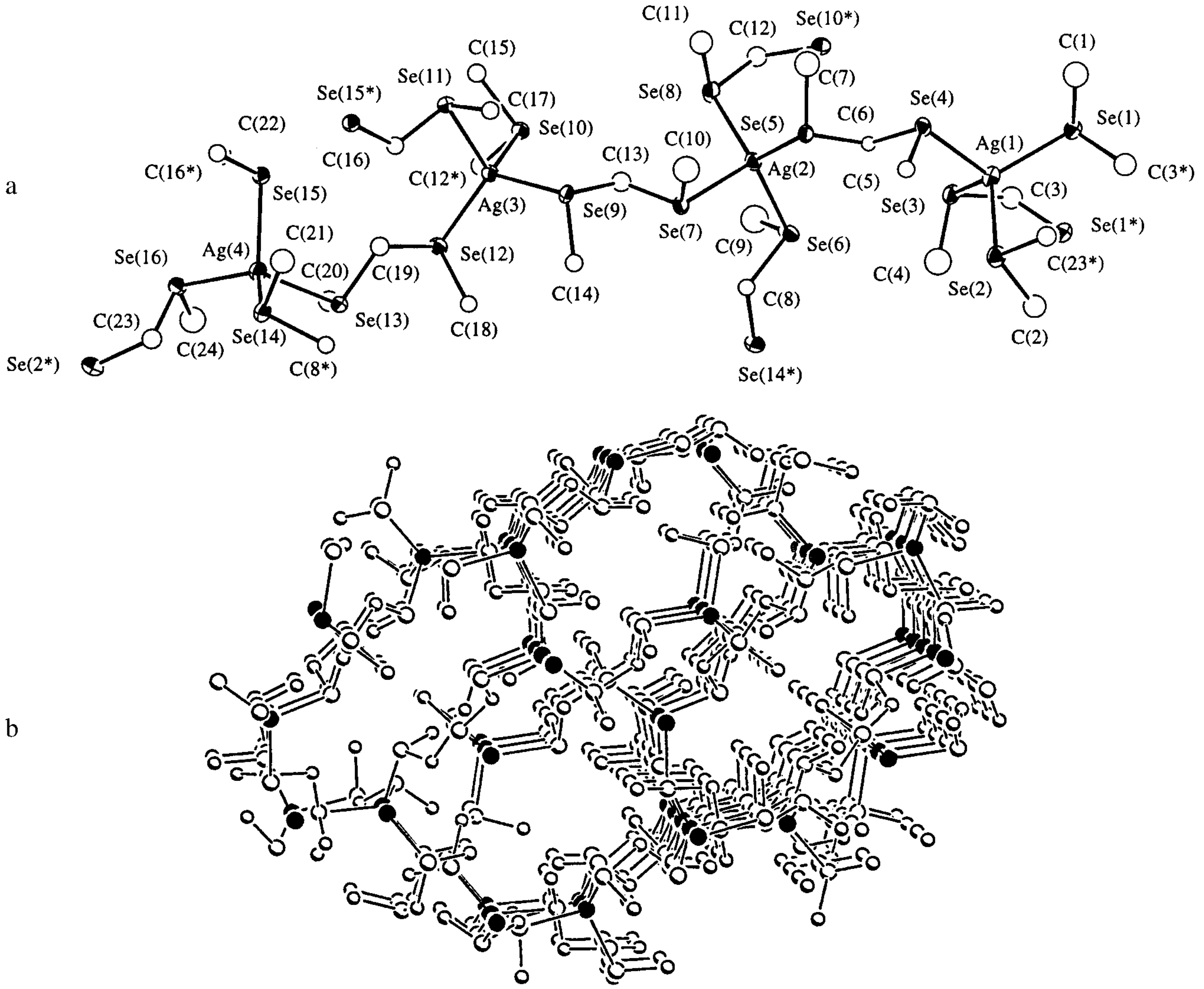

Figure 2. (a) View of tetranuclear cation fragment, $[Ag_4(MeSeCH_2SeMe)_8]^{4+}$, in the asymmetric unit showing the numbering scheme adopted and the nearest symmetry related neighbors (marked by an asterisk). H-atoms are omitted for clarity. (b) View down the *b*-axis of the polymeric 3-D network formed by $[Ag_n(MeSeCH_2SeMe)_{2n}](BF_4)_n$ illustrating the channels formed. Ag atoms are shaded; H-atoms are omitted for clarity.

for three of the F atoms. Thus, around B(4) there is one fully occupied F atom, F(13) and six 50% occupied F atoms, F(14)−F(19). At isotropic convergence the raw data were corrected for absorption using DIFABS.[31] The Ag, Se, B, and all fully occupied F atoms were refined anisotropically, while H atoms were included in fixed, calculated positions.

Results and Discussion

The silver(I) and copper(I) complexes were prepared by the reaction of the appropriate starting material, $AgBF_4$ or $[Cu(MeCN)_4]PF_6$, with 2 molar equiv of ligand in dichloromethane under a N_2 atmosphere. The compounds were precipitated by pouring the reaction solution into stirred diethyl ether. All of the silver and copper complexes were air stable white, or pale yellow in the case of the telluroether complexes, powders. The silver complexes were found to be mildly light sensitive as solids and more sensitive in solution, thus samples were stored in the aluminium foil wrapped containers in a freezer. IR spectroscopy (CsI disks) indicated the presence of the appropriate counterion, BF_4^- or PF_6^-, and the presence of ligand within the complexes.

FAB mass spectra showed the presence of prominent fragments $[Ag_2(L\text{-}L)_2(BF_4)]^+$, $[Ag(L\text{-}L)_2]^+$, and $[Ag(L\text{-}L)]^+$ in addition to species arising from fragmentation of the ligands, for the silver complexes. The presence of dimetallic ions are in marked contrast to spectra of the copper complexes in this study, which showed only $[Cu(L\text{-}L)_2]^+$, and $[Cu(L\text{-}L)]^+$ fragments, and the previously reported silver(I) and copper(I) complexes with di- and trimethylene backboned ligands $\{RE(CH_2)_nER\}$ ($n = 2, 3$) which showed only mononuclear fragments in their FAB mass spectra.[9,32]

X-ray Crystallographic Studies. In order to establish whether these new materials did indeed adopt extended frameworks as we had proposed, single-crystal X-ray diffraction studies were undertaken on certain examples. Crystals of suitable quality for single-crystal X-ray diffraction studies were grown by vapour diffusion of diethyl ether into either CH_3NO_2 $\{[Cu_n(MeSCH_2SMe)_{2n}](PF_6)_n{\cdot}n MeNO_2$ and $[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n\}$ or CH_2Cl_2 $\{[Ag_n(MeSeCH_2SeMe)_{2n}](BF_4)_n\}$ solutions of the complexes.

The crystal structure of $[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$ shows tetrahedrally coordinated Cu(I) ions, bonded to one Se donor from each of four distinct diselenoether ligands. Importantly, the second Se donor of each ligand is ligated to a *different* adjacent Cu(I) ion to give an infinite 3-D cationic network as we had proposed, (Tables 2 and 3, Figure 1). Furthermore, this

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(31) Walker, N.; Stuart, D. DIFABS: An empirical Absorption Correction Program. *Acta. Crystallogr. Sect. A* **1983**, *39*, 158.

(32) Black, J. R.; Levason, W. *J. Chem. Soc., Dalton Trans.* **1994**, 3225.

Table 5. Fractional Atomic Coordinates for $[Ag_n(MeSeCH_2SeMe)_{2n}](BF_4)_n$

atom	*x*	*y*	*z*
Ag(1)	0.8816(2)	0.4438(2)	0.42647(9)
Ag(2)	0.8562(2)	0.0569(2)	0.30600(9)
Ag(3)	0.6919(2)	−0.3270(2)	0.15768(9)
Ag(4)	0.4118(2)	−0.6979(2)	0.06727(9)
Se(1)	1.0039(2)	0.5776(2)	0.4550(1)
Se(2)	0.7121(2)	0.4524(2)	0.4493(1)
Se(3)	0.9745(2)	0.2890(2)	0.4560(1)
Se(4)	0.8339(2)	0.4230(2)	0.3366(1)
Se(5)	0.7977(2)	0.2273(2)	0.2830(1)
Se(6)	0.8723(2)	0.0107(2)	0.3928(1)
Se(7)	0.6989(2)	−0.0333(2)	0.2678(1)
Se(8)	0.9880(2)	−0.0074(2)	0.2652(1)
Se(9)	0.6214(2)	−0.1741(2)	0.1856(1)
Se(10)	0.8789(2)	−0.3339(2)	0.1892(1)
Se(11)	0.6658(2)	−0.2937(2)	0.0673(1)
Se(12)	0.6374(2)	−0.4858(2)	0.1881(1)
Se(13)	0.4764(2)	−0.6400(2)	0.1516(1)
Se(14)	0.2362(2)	−0.6333(2)	0.0516(1)
Se(15)	0.5138(2)	−0.6257(2)	0.0109(1)
Se(16)	0.4346(2)	−0.8779(2)	0.0560(1)
F(1)	0.816(1)	0.139(2)	0.5654(8)
F(2)	0.704(2)	0.172(2)	0.605(1)
F(3)	0.843(2)	0.134(2)	0.6398(9)
F(4)	0.752(2)	0.026(2)	0.6021(9)
F(5)	0.228(2)	0.233(1)	0.6743(8)
F(6)	0.354(1)	0.320(2)	0.6755(8)
F(7)	0.214(1)	0.373(1)	0.6435(8)
F(8)	0.251(1)	0.356(1)	0.7187(7)
F(9)	0.659(1)	0.357(1)	0.8400(7)
F(10)	0.557(1)	0.276(1)	0.8721(7)
F(11)	0.708(1)	0.268(1)	0.8999(8)
F(12)	0.633(1)	0.397(1)	0.9099(7)
F(13)	0.173(1)	0.132(2)	0.9269(8)
F(14)	0.222(3)	0.060(4)	0.867(2)
F(15)	0.196(3)	0.142(3)	0.862(1)
F(16)	0.085(4)	0.142(4)	0.851(2)
F(17)	0.055(3)	0.094(3)	0.876(2)
F(18)	0.119(3)	0.006(3)	0.896(2)
F(19)	0.188(4)	−0.004(4)	0.887(2)
C(1)	1.003(3)	0.659(3)	0.405(1)
C(2)	0.722(2)	0.446(2)	0.515(1)
C(3)	1.059(2)	0.337(2)	0.511(1)
C(4)	0.888(3)	0.228(3)	0.486(1)
C(5)	0.699(2)	0.421(2)	0.326(1)
C(6)	0.853(2)	0.290(2)	0.336(1)
C(7)	0.868(3)	0.280(3)	0.241(1)
C(8)	0.760(2)	−0.067(2)	0.391(1)
C(9)	0.956(3)	−0.085(3)	0.392(2)
C(10)	0.653(3)	0.056(3)	0.222(1)
C(11)	0.965(2)	0.056(3)	0.208(1)
C(12)	1.113(2)	0.042(2)	0.291(1)
C(13)	0.731(2)	−0.129(2)	0.231(1)
C(14)	0.545(2)	−0.206(2)	0.229(1)
C(15)	0.913(2)	−0.355(2)	0.129(1)
C(16)	0.561(2)	−0.375(2)	0.051(1)
C(17)	0.597(2)	−0.179(2)	0.069(1)
C(18)	0.546(2)	−0.452(2)	0.225(1)
C(19)	0.551(2)	−0.535(2)	0.137(1)
C(20)	0.576(2)	−0.718(2)	0.176(1)
C(21)	0.237(2)	−0.528(2)	0.012(1)
C(22)	0.599(2)	−0.724(2)	0.002(1)
C(23)	0.309(2)	−0.916(2)	0.055(1)
C(24)	0.490(3)	−0.932(3)	0.111(1)
B(1)	0.785(3)	0.120(3)	0.604(2)
B(2)	0.261(3)	0.324(3)	0.678(2)
B(3)	0.640(3)	0.327(3)	0.881(1)
B(4)	0.148(4)	0.095(4)	0.886(2)

Table 6. Selected Bond Lengths (Å) and angles (deg) for $[Cu_n(MeSCH_2SMe)_{2n}]^{n+}$

Cu(1)−S(1)	2.322(4)	Cu(1)−S(2)	2.311(4)
Cu(1)−S(3)	2.342(4)	Cu(1)−S(4)	2.327(4)
S(1)−C(1)	1.82(1)	S(1)−C(2)	1.81(1)
S(2)−C(3)	1.80(1)	S(2)−C(4)	1.82(1)
S(3)−C(4)	1.81(1)	S(3)−C(5)	1.81(1)
S(4)−C(2)	1.82(1)	S(4)−C(6)	1.78(1)
S(1)−Cu(1)−S(2)	121.0(1)	S(1)−Cu(1)−S(3)	107.7(1)
S(1)−Cu(1)−S(4)	102.9(1)	S(2)−Cu(1)−S(3)	102.3(1)
S(2)−Cu(1)−S(4)	107.8(1)	S(3)−Cu(1)−S(4)	116.0(1)
Cu(1)−S(1)−C(1)	114.9(5)	Cu(1)−S(1)−C(2)	102.1(5)
C(1)−S(1)−C(2)	101.1(6)	Cu(1)−S(2)−C(3)	113.0(4)
Cu(1)−S(2)−C(4)	102.7(4)	C(3)−S(2)−C(4)	100.1(6)
Cu(1)−S(3)−C(4)	115.9(4)	Cu(1)−S(3)−C(5)	111.6(4)
C(4)−S(3)−C(5)	100.7(6)	Cu(1)−S(4)−C(2)	114.0(5)
Cu(1)−S(4)−C(6)	112.3(5)	C(2)−S(4)−C(6)	100.5(7)
S(2)−C(4)−S(3)	106.5(6)	S(1)−C(2)−S(4)	106.9(7)

Table 7. Fractional Atomic Coordinates for $[Cu_n(MeSCH_2SMe)_{2n}](PF_6)\cdot nMeNO_2$

atom	*x*	*y*	*z*
Cu(1)	0.82863(10)	0.2151(2)	0.37587(7)
S(1)	0.9024(2)	0.3673(4)	0.3180(1)
S(2)	0.9020(2)	0.0666(3)	0.4344(1)
S(3)	0.7475(2)	0.3706(4)	0.4302(1)
S(4)	0.7501(3)	0.0580(3)	0.3217(1)
P(1)	0.5000	0.0000	0.5000
P(2)	0.5000	0.4116(7)	0.2500
F(1)	0.5814(5)	0.0562(10)	0.5318(4)
F(2)	0.4393(6)	0.034(1)	0.5470(4)
F(3)	0.4827(7)	0.161(1)	0.4785(5)
F(4)	0.5860(8)	0.411(1)	0.2194(5)
F(5)	0.4460(8)	0.412(1)	0.1992(4)
F(6)	0.5000	0.237(1)	0.2500
F(7)	0.5000	0.586(1)	0.2500
O(1)	0.8475(8)	0.296(2)	0.6252(7)
O(2)	0.7235(8)	0.178(1)	0.6539(5)
N(1)	0.7830(8)	0.163(1)	0.6225(6)
C(1)	1.0172(9)	0.385(1)	0.3304(5)
C(2)	0.8647(9)	0.552(1)	0.3359(5)
C(3)	1.0155(9)	0.052(1)	0.4203(5)
C(4)	0.8668(8)	−0.121(1)	0.4169(5)
C(5)	0.7466(9)	0.302(1)	0.4961(5)
C(6)	0.7480(9)	0.124(1)	0.2566(6)
C(7)	0.7922(8)	0.067(1)	0.5930(5)

network contains large channels which incorporate the PF_6^- counter anions. These channels have six copper atoms around their periphery, leading to an approximately cylindrical shape of diameter ca. 12.5 Å. The Cu−Se distances are within the range 2.40−2.46 Å and these compare well with those distances reported for the macrocyclic selenoether complex $[Cu([16]aneSe_4)](SO_3CF_3)$ d(Cu−Se) = 2.42−2.52 Å,[19] ($[16]aneSe_4$ = 1,5,9,13-tetraselenacyclohexadecane). The Se−Cu−Se angles in the $[Cu(MeSeCH_2SeMe)_2]^+$ fragment are close to tetrahedral. In an effort to establish whether this type of extended cationic framework is a general phenomenon for the compounds being studied, we also investigated the solid state structure of the silver(I) selenoether analogue. The crystal structure of $[Ag_n(MeSeCH_2SeMe)_{2n}](BF_4)_n$ does in fact turn out to be similar to that of $[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$ in that it shows (Tables 4 and 5, Figure 2) tetrahedral Ag(I) ions coordinated to one Se donor from each of four distinct diselenoether ligands, with the other Se donor being ligated to an adjacent Ag(I) ion to give an infinite 3-D cationic network. However, the asymmetric unit has a tetranuclear silver chain as shown in Figure 2a, and these chains are interconnected in such a manner that each chain crosses other chains throughout the infinite 3-D lattice. As with the corresponding copper complex described above, the 3-D structure adopted generates channels in which the counterions, in this case BF_4^-, are incorporated. However, in contrast to $[Cu_n(MeSeCH_2SeMe)_{2n}](PF_6)_n$ these channels have a total of eight silver units around their periphery leading to rectangular-

Table 8. Multinuclear NMR Data

	δ(^{77}Se or ^{125}Te)/ppm[b]		δ(^{63}Cu or ^{109}Ag)/ppm[c]		
complex[a]	300 K	245 K	300 K	245 K	Comment
[Cu{$MeSCH_2SMe$}$_2$]PF_6			+58 (6900)	94 (3350)	^{63}Cu signal only with excess L-L
[Ag{$MeSCH_2SMe$}$_2$]BF_4			+678		^{109}Ag δ +796 with excess L-L
[Cu{$MeSeCH_2SeMe$}$_2$]PF_6	+101	+90	−42 (2800)	−32 (2800)	^{63}Cu signal only with excess L-L
[Ag{$MeSeCH_2SeMe$}$_2$]BF_4	+139		+ 723		^{109}Ag δ +822 with excess L-L
[Cu{$MeTeCH_2TeMe$}$_2$]PF_6	+151		−50 (3500)	−44 (3000)	^{63}Cu signal only with excess L-L
[Ag{$MeTeCH_2TeMe$}$_2$]BF_4	+212		n.o. (see text)[d]		

[a] Recorded in $MeNO_2/(CD_3)_2CO$. [b] Relative to external neat Me_2Se or Me_2Te at 300 K; free ligands $MeSeCH_2SeMe$ $\delta = +117$, $MeTeCH_2TeMe$ $\delta = +212$. [c] Relative to $[Cu(MeCN)_4]^+$ in $MeCN/CD_3CN$ at 300 K or to 9.1 mol dm^3 solution of Ag^+ in H_2O/D_2O as appropriate. For ^{63}Cu spectra $w_{1/2}$/Hz in parentheses. [d] n.o. = not observed.

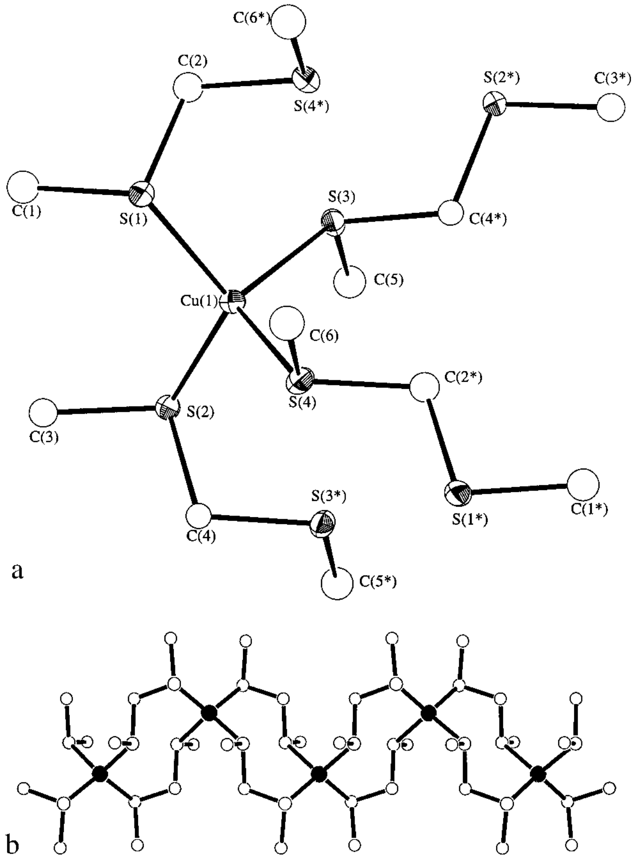

Figure 3. (a) View of mononuclear cation fragment, $[Cu(MeSCH_2SMe)_2]^+$, in the asymmetric unit showing the numbering scheme adopted and the nearest symmetry related neighbors (marked by an asterisk). (b) View of a portion of the cationic polymer chain structure formed by $[Cu_n(MeSCH_2SMe)_{2n}]^{n+}$. Cu atoms are shaded; H-atoms are omitted for clarity.

shaped channels of cross section ca. 12.6 × 4.1 Å. The Ag-Se bond lengths are comparable with those observed in $[Ag_n(PhSeCH_2CH_2CH_2SePh)_{2n}](BF_4)_n$, d(Ag−Se) = 2.643−2.695 Å (range) and $[Ag(MeSeCH_2CH_2SeMe)_2]BF_4$, d(Ag-Se) = 2.610−2.638 Å (range).[9] The angles around the silver atoms in the new framework structure are in the range 98.2−120.3°.

To our surprise, the copper(I) thioether species $[Cu_n(MeSCH_2SMe)_{2n}](PF_6)_n \cdot nMeNO_2$ adopts a rather different structure, showing tetrahedrally coordinated Cu(I) ions bonded to one of the S-donors of four distinct dithioether ligands. In this case the other S-donors of the ligands are ligated to adjacent Cu(I) ions to form 8-membered rings incorporating two bridging ligands and two Cu atoms in a chair-like arrangement. These rings are linked to each other via the Cu centers, giving a cationic ribbon-like arrangment, (Tables 6 and 7, Figure 3). The tetrahedral geometry at Cu(I) results in the rings alternating at approximately 90° to each other along the linear chain. The Cu−S bond lengths at 2.31−2.34 Å are similar to those in $[Cu(EtSCH_2CH_2SEt)_2]BF_4$ Cu−S = 2.303(5) Å average,[33] and $[Cu(MeSCH_2CH_2SMe)_2]ClO_4$, Cu−S = 2.263(6) Å.[34] The S−Cu−S angles in $[Cu_n(MeSCH_2SMe)_{2n}]^{n+}$ are close to tetrahedral and the discrete PF_6^- counterions and $MeNO_2$ solvent molecules in the lattice lie on the periphery of the cationic chain. The overall structure then contrasts with the copper(I) and silver(I) selenoether complexes described above.

Multinuclear NMR Studies. The complexes were studied in solution by the use of multinuclear NMR spectroscopy, using $MeNO_2/CD_3NO_2$ as solvent to permit comparison with our previous study[9] of the $RE(CH_2)_3ER$ systems. We anticipated that as these species were derived from complexes of d^{10} metal ions, the polymeric structures observed in the solid state would not persist in solution, but would break down to smaller fragments.

The ^{1}H NMR spectra of all the complexes show single δ(CH_3) and δ(CH_2) resonances, typical of fast exchange.[9,32] Both ^{77}Se{^{1}H} and ^{125}Te{^{1}H} NMR spectra of the complexes in $MeNO_2$ exhibited single resonances (Table 8). Addition of the appropriate free ligand to these solutions resulted in these single resonances shifting, confirming fast exchange. In the Cu(I) and Ag(I) complexes of $RE(CH_2)_nER$ (E = Se or Te, n = 2, 3) the ^{77}Se and ^{125}Te shifts were to low frequency of the free ligand resonance, the opposite of that observed with most metal complexes,[9] and attributed to the effects of the electron-rich d^{10} metal centers. In the present complexes (Table 8) the two copper(I) complexes conform to this pattern, but curiously the silver(I) complex of $MeSeCH_2SeMe$ shows a small high frequency coordination shift, while the ^{125}Te resonance of $[Ag_n(MeTeCH_2TeMe)_{2n}](BF_4)_n$ is not shifted from the free ligand value, although the peak is much broader. Further information about the species present in solution came from the ^{63}Cu and ^{109}Ag NMR data.

^{63}Cu has a spin $I = {}^3/_2$ {69%, Ξ = 26.528 MHz, D_c = 365, quadrupole moment = 0.211×10^{-28} m^2} and the observation of NMR signals is determined by two main factors: first, the rate of quadrupolar relaxation and, second, the nature and rate of exchange processes occurring in solution.[32,35] In essence, for a ^{63}Cu NMR signal to be observed, the ^{63}Cu nucleus must be within an approximately tetrahedral environment. For the copper complexes studied here no signal was observed over the temperature range 300−245 K in $MeNO_2$ solution. Since chelation by the $MeECH_2EMe$ ligands is unlikely and, with the stoichiometry Cu:L-L 1:2, the average coordination number of the copper in these solutions will be less than four. Addition of a large excess of the appropriate ligand resulted in the appearance of a ^{63}Cu resonance in each case (Table 8), with

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(33) Baker, E. N.; Norris, G. E. *J. Chem. Soc., Dalton Trans.* **1977**, 877.
(34) Olmstead, M. M.; Musker, W. K.; Kessler, R. M. *Inorg. Chem.* **1981**, *20*, 151.
(35) Black, J. R.; Levason, W.; Spicer, M. D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1993**, 3129.

shifts similar to those reported for $[Cu(EMe_2)_4]^+$ ions[32], indicative of the formation of $[Cu(\eta^1\text{-}MeECH_2EMe)_4]^+$ species.

Silver-109 has $I = {}^1/_2$ but direct observation is difficult due to its low magnetogyric ratio, low receptivity and long relaxation times. In our previous work[9] we have established that $Ag(S/Se/Te)_4^+$ species have ^{109}Ag resonances in the range *ca.* 900–1100 ppm. For $[Ag_n(MeSCH_2SMe)_{2n}]^{n+}$ in $MeNO_2$ the ^{109}Ag resonance was at $\delta = 678$, not unreasonable for a species in which the silver is on average coordinated to two thioether donors. On addition of a 5-fold excess of $MeSCH_2SMe$, the resonance shifted to $\delta = 796$, still a rather lower frequency than expected for an AgS_4^+ species. Similar behavior was observed for the $[Ag_n(MeSeCH_2SeMe)_{2n}]^{n+}$ complex (Table 8). It is possible that even with a large excess of ligand the average coordination number of the silver complexes is less than four. Unfortunately the $[Ag_n(MeTeCH_2TeMe)_{2n}](BF_4)_n$ complex was unstable in solution and rapidly decomposed even in the dark, which prevented a ^{109}Ag spectrum being obtained.

Conclusions

These results show that unprecedented networks incorporating large channels[36] can be constructed using silver(I) and copper(I) complexes of methylene bridged thio-, seleno-, and telluroether ligands, the precise structural features of which are subtley dependent upon the ligand donor atom type and the nature of the anion used. Further work will include studies to determine whether the cavity sizes in these materials can also be controlled through variation of the ligand substituents.

Acknowledgment. We thank the University of Southampton for support and the EPSRC for a grant to purchase the diffractometer.

Supporting Information Available: Tables S1–S13, containing crystallographic data and refinement parameters, atomic coordinates, anisotropic thermal parameters and full listings of bond lengths and angles for the three structures, (15 pages). Ordering information is given on any current masthead page.

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(36) Although Figures 1b and 2b show the metal centers aligned, the closest M···M distance along this direction is greater than 9 Å for both systems, indicating that there is no direct metal–metal interaction.