Inorg. Chem. **1995**, *34*, 3755−3759

Synthesis and Characterization of Polymeric Ag(I)−Telluroether and Cu(I)−Diorganyl Ditelluride Complexes: Crystal Structures of $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$, $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$, and $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$

Wen-Feng Liaw,[*,†] Chia-Huei Lai,[†] Show-Jen Chiou,[†] Yih-Chern Horng,[†] Chin-Cheng Chou,[†] Ming-Chi Liaw,[†,‡] Gene-Hsiang Lee,[‡] and Shie-Ming Peng[‡]

Department of Chemistry, National Changhua University of Education, Changhua, Taiwan, and Department of Chemistry, National Taiwan University, Taipei, Taiwan

Received September 15, 1994[®]

Reaction of ligand $MeTe(CH_2)_3TeMe$ with $AgBF_4$ in CH_3CN produced the light-sensitive polymeric coordination complex $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$. This compound crystallized in the monoclinic space group $P2_1/n$ with $a = 8.755(3)$ Å, $b = 20.441(8)$ Å, $c = 12.227(3)$ Å, $\beta = 103.13(3)°$, $V = 2130.9(12)$ Å^3, $Z = 4$, $F(000) = 1504$. Final $R = 0.057$ and $R_w = 0.062$ resulted from refinement of 2776 total reflections with 154 parameters. Reaction of $(Te(p\text{-}C_6H_4F))_2$ and $AgBF_4$ in acetonitrile at ambient temperature generated red, light-sensitive $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$, a homodiorganyl ditelluride doubly-bridged complex. Crystal data: triclinic space group $P\bar{1}$, $a = 6.835(2)$ Å, $b = 13.255(2)$ Å, $c = 13.824(4)$ Å, $\alpha = 116.48(3)°$, $\beta = 95.95(2)°$, $\gamma = 98.90(2)°$, $V = 1086.2(4)$ Å^3, $Z = 1$, $\varrho_{calcd} = 2.165$ g cm^{-3}, $\mu = 36.13$ cm^{-1}, $F(000) = 668$. Refinement of 3807 reflections and 254 parameters gave $R = 0.027$ and $R_w = 0.028$. Treatment of $(MeTe)_2$ with CuCl in CH_3CN at ambient temperature yielded polymeric $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$. Crystal data: monoclinic space group $P2_1/c$, $a = 9.923(2)$ Å, $b = 8.091(2)$ Å, $c = 10.232(3)$ Å, $\beta = 116.01(2)°$, $V = 738.3(3)$ Å^3, $Z = 2$, $F(000) = 668$. Refinement of 949 reflections and 56 parameters gave $R = 0.027$ and $R_w = 0.025$.

Introduction

The anionic Fe(0)−chalcogenolate species $[PhEFe(CO)_4]^-$ (E = Te, Se) is an effective template for preparation of Fe(II)−chalcogenolate $[Fe(CO)_3(EPh)_3(E'Ph)_{3-n}]^-$ (n = 0, 1, 2, 3; E = Te, E′ = Se) and Fe−telluroether $(PhTeMe)Fe(CO)_4/Fe(CO)_3(PhTeMe)(TePh)_2$ complexes.[1,2] Here we describe our efforts to extend the chemistry to d^{10} Ag(I)−telluroether, −diorganyl ditelluride and Cu(I)−diorganyl ditelluride, using the d^{10} metal cations to link organyl telluroether chains or diorganyl ditellurides. Although many telluroether (TeR_2) complexes of Ag(I) and Cu(I) are prepared and characterized with respect to industrial application on photothermographic imaging elements and the bonding mode of monodentate telluroether ligands,[3−5] polymeric $[Ag(RTe(CH_2)_3TeR)_m]_n[BF_4]_n$, $[Ag_2(NCCH_3)_4(\mu_2\text{-}RTeTeR)_2][BF_4]_2$, and polymeric $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$ are not reported.[3,6] The analogs $[(\mu\text{-}RTeTeR)Cu(\mu\text{-}Cl)]_n$ (R = Et, n-Bu, n-C_5H_{11}) were proposed to have a polymeric structure on the basis of infrared and Mössbauer spectra[6a] and were reported to decompose on attempted recrystallization.

We noticed the emergence of the $RTe(CH_2)_3TeR$ and RTeTeR species as promising ligands with both high multidenticity and bonding flexibility.[6,7] Here we report the synthesis and characterization of $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$, $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$, and $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$ obtained by combining $AgBF_4$/CuCl with appropriate multifunctional ligands, $MeTe(CH_2)_3TeMe$ and RTeTeR ($R = p\text{-}C_6H_4F$, Me). The complex $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ presents a polymeric species in which each Ag(I) metal is strongly bound to tellurium atoms. In complex $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$, the silver cation Ag(I) and bis(fluorophenyl) ditelluride exhibit an interesting mode of coordination.

Results and Discussion

Synthesis. The reaction between $AgBF_4$ and $MeTe(CH_2)_3TeMe$ in a 1:2 ratio occurred rapidly in CH_3CN in a dark environment at ambient temperature to produce an orange-

---

[†] National Changhua Universityof Education.

[‡] National Taiwan University.

[®] Abstract published in *Advance ACS Abstracts*, June 1, 1995.

(1) (a) Liaw, W.-F.; Chiang, M.-H.; Liu, C.-J.; Harn, P.-J.; Liu, L.-K. *Inorg. Chem.* **1993**, *32*, 1536. (b) Liaw, W.-F.; Lai, C.-H.; Chiang, M.-H.; Hsieh, C.-K.; Lee, G.-H.; Peng, S.-M. *J. Chin. Chem. Soc. (Taipei)* **1993**, *40*, 437.

(2) (a) Liaw, W.-F.; Chiang, M.-H.; Lai, C.-H.; Chiou, S.-J.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **1994**, *33*, 2493. (b) Liaw, W.-F.; Chiou, S.-J.; Lee, W.-Z.; Lee, G.-H.; Peng, S.-M. *J. Chin. Chem. Soc. (Taipei)* **1993**, *40*, 361. (c) Liaw, W.-F.; Ou, D.-S.; Horng, Y.-C.; Lai, C.-H.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **1994**, *33*, 2495.

(3) (a) Gysling, H. J. *Coord. Chem. Rev.* **1982**, *42*, 133. (b) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365. (c) Hope, E. G.; Levason, W. *Coord. Chem. Rev.* **1993**, *122*, 109.

(4) (a) Calderazzo, F.; Vitali, D.; Poli, R.; Atwood, J. L.; Rogers, R. D.; Lummings, J. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1004. (b) Matsuzaka, H.; Ogino, T.; Nishio, M.; Hidai, M.; Nishibayashi, Y.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1994**, 223.

(5) (a) Coates, G. E. *J. Chem. Soc.* **1951**, 2003. (b) Davies, I.; McWhinnie, W. R. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 763.

(6) (a) Davies, I.; McWhinnie, W. R.; Dance, N. S.; Jones, C. H. W. *Inorg. Chim. Acta* **1978**, *29*, L217. (b) Cobbledick, R. E.; Einstein, F. W. B.; McWhinnie, W. R.; Musa, F. H. *J. Chem. Res. Synop.* **1979**, 145. (c) Cobbledick, R. E.; Einstein, F. W. B.; McWhinnie, W. R.; Musa, F. H. *J. Chem. Res., Miniprint* **1979**, 1901. (d) Davies, I.; McWhinnie, W. R.; Dance, N. S.; Jones, C. H. W. *Inorg. Chim. Acta* **1978**, *29*, L203. (e) McWhinnie, W. R.; Rattanaphani, V. *Inorg. Chim. Acta* **1974**, *9*, 153.

(7) (a) Hope, E. G.; Kemmitt, T.; Levason, W. *Organometallics* **1987**, *6*, 207. (b) Kemmitt, T.; Levason, W.; Webster, M. *Inorg. Chem.* **1989**, *28*, 692. (c) Pathirana, H. M. K. K.; Downs, A. W.; McWhinnie, W. R.; Granger, P. *Inorg. Chim. Acta* **1988**, *143*, 161. (d) Singh, A. K.; Srivastava, V. *J. Coord. Chem.* **1992**, *27*, 237. (e) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1985**, *287*, 345. (f) Abel, E. W.; Beckett, M. A.; Orrell, K. G.; Sik, V.; Stephenson, D.; Singh, H. B.; Sudha, N. *Polyhedron* **1988**, *7*, 1169. (g) Khandelwal, B. L.; Kundu, K.; Gupta, S. K. *Inorg. Chim. Acta* **1988**, *154*, 183. (h) Jones, C. H. W.; Sharma, R. D. *Organometallics* **1986**, *5*, 805.

0020-1669/95/1334-3755$09.00/0

yellow solid (92% yield), which was recrystallized from acetonitrile−ether as light orange-yellow crystals of $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ (eq 1). Additionally, when the same reaction were carried out in 1:3 or 1:4 ($AgBF_4$:$MeTe(CH_2)_3TeMe$) ratio under similar experimental conditions, the same product $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ was obtained after being recrystallized from acetonitrile-ether. The compound of unusual composition, $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$, is a polymer containing distorted tetrahedral $[Ag(MeTe(CH_2)_3TeMe)_2]^+$ units connected through ditelluroether chain $MeTe(CH_2)_3TeMe$ bridges to form layers. Polymeric $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ is extremely sensitive to light. Exposure of the light orange-yellow solids to sunlight for a few seconds leads to a black powder that is insoluble in any organic solvent, presumably consisting of silver telluride compound. Storage of this complex at −10 °C in the dark prevents decomposition over the course of at least several weeks.

$$AgBF_4 + 2MeTe(CH_2)_3TeMe \rightarrow [Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n \quad (1)$$

The polymeric orange-yellow solid is insoluble in most hydrocarbon solvents, such as hexane, THF, dichloromethane and ether, but shows slight solubility in acetonitrile, which allows the solution NMR experiments to be performed. In the ^1H NMR spectrum, a singlet appears for the methyl protons (MeTe-) at δ 2.08, and weak satellites of the singlet line at a separation 17.6 Hz are observed. The occurrence of one sharp triplet (δ 2.82 ($J = 6.0$ Hz)) and another sharp quintet (δ 2.20 ($J = 6.0$ Hz)) ^1H NMR resonance were assigned to the $TeCH_2$- protons and $TeCH_2CH_2$- protons individually. This compound also displayed three distinct signals (−15.5, 8.9, 29.2 ppm) in the ^{13}C NMR spectra, consistent with the presence of four equivalent $MeTe(CH_2)_3TeMe$ groups in the ^{13}C NMR spectrum of $[Ag(MeTe(CH_2)_3TeMe)_2]_n [BF_4]_n$ in acetonitrile solution. On the basis of ^1H and ^{13}C NMR spectroscopy, it is assumed that the structural feature (polymeric structure) found for $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ in the solid state is retained in acetonitrile solution.[8] Although we cannot unambiguously rule out the possibility of formation of the monomer ditelluroether bidentate complex $[Ag(MeTe(CH_2)_3TeMe)_2][BF_4]$ in acetonitrile solution. The ^{125}Te NMR spectrum shows only one signal at 24.4 ppm, at a smaller chemical shift than that of the free $MeTe(CH_2)_3TeMe$ ligand at 105.3 ppm. The most likely explanation for this chemical shift is that there is significant electron donation from d^{10} Ag(I) to the metal-bound tellurium atoms to cause significant shielding of the ^{125}Te nuclei.[3]

As illustrated in eq 2, treatment of $(Te(p\text{-}C_6H_4F))_2$ with $AgBF_4$ in equimolar proportions in acetonitrile at ambient temperature leads to formation of a homodiorganyl ditelluride doubly-bridged complex $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$ in 96% isolated yield. This reaction is rapid at room temperature and is completed within 30 min.

$$2(Te(p\text{-}C_6H_4F))_2 + 2AgBF_4 \xrightarrow{CH_3CN} [Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2 \quad (2)$$

The compound is strongly colored and sensitive to light; the crystalline solid was easily crystallized from acetonitrile/ether at −10 °C. At room temperature, the product is stable and can be kept in hexane under nitrogen for prolonged periods. Some decomposition was observed over a 2 h period while refluxing in CH_3CN. To evaluate the influence of phenyl vs alkyl groups on their reactivity with Ag^+, we surveyed the reactivity of RTeTeR (*R* = Ph, Me) toward $AgBF_4$. An immediate reaction ensued when RTeTeR was added to a solution of $AgBF_4$ in acetonitrile at room temperature. However, the products partially decomposed under vacuum at ambient temperature. We observed no indication of formation of a Cu−diorganyl ditelluride complex in the reaction of $[Cu(CH_3CN)_4][ClO_4]$ and bis(*p*-fluorophenyl) ditelluride/diphenyl ditelluride under the same reaction conditions on the basis of NMR spectra. These results clearly indicate that $[Ag(CH_3CN)_4][BF_4]$ is significantly more reactive than $[Cu(CH_3CN)_4][ClO_4]$ for a coordination reaction of this type.

The facile synthesis of $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$ under mild reaction conditions in good yield presages access to other interesting d^{10} transition-metal compounds. Reaction of CuCl with MeTeTeMe in CH_3CN at ambient temperature afforded red-brown crystals $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$ in ca. 85% yield after recrystallization from acetonitrile and ether (eq 3). The property of insolubility in common organic solvents except acetonitrile indicates that the red-brown product is highly polymeric.

$$CuCl + MeTeTeMe \rightarrow [(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n \quad (3)$$

The proposed polymeric structure $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$ was confirmed by single-crystal X-ray diffraction. ^{125}Te NMR spectra were obtained on polymeric $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$ to investigate the extent to which the Cu(I) electronically affects the tellurium atoms. In acetonitrile-d_3 at 298 °K, the ^{125}Te chemical shift for $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$ showed the expected single signal at 30.0 ppm. This upfield chemical shift occurs for tellurium bonded to d^{10} CuCl species, which has a chemical shift of metal-bound ^{125}Te smaller than that of tellurium nuclei in $(MeTe)_2$.[7a]

Structure of $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$. Single crystals of polymeric $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ suitable for X-ray crystallography were formed by slow diffusion of diethyl ether into $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ acetonitrile solution at −10 °C. The complex contains cationic $[Ag(MeTe(CH_2)_3TeMe)_2]_n$ layers and noninteracting $[BF_4]_n$ anions situated between the layers (Figure 1). Alternatively, the Ag(I) polymer bridged by $MeTe(CH_2)_3TeMe$ ligands is envisaged to be linked by the repeat unit of a $Ag_4(MeTe(CH_2)_3TeMe)_4$ ring. This coordination polymer is the first example of a Ag(I) complex containing bridging ditelluroether ligands.[3,7d] In $[Ag(MeTe(CH_2)_3TeMe)_2]_n$ cations, each Ag(I) atom is coordinated by four tellurium atoms of four bridging $MeTe(CH_2)_3TeMe$ chains to give a four-coordinate distorted tetrahedral Ag(I) center with Te−Ag−Te bond angles 122.5(1)°, 111.6(1)°, 105.0(1)°, 106.5(1)°, 99.5(1)°, and 110.9(1)°.

The Ag−Te bond lengths fall into two groups: shorter distances 2.789(2) and 2.785(2) Å and longer distances 2.820(2) and 2.837(2) Å. The range of Ag−Te distances observed in this polymeric compound, 2.785(2)−2.837(2) Å, is comparable with Ag−Te distances in other complexes containing Ag−tellurolate, $[Ag_4(TeR)_6]^{2-}$ (*R* = thienyl, average 2.754(5) Å),[9] and Ag−telluride, $[AgTe_7]^{2-}$ (2.695(2)−2.725(2) Å).[10a]

---

(8) (a) Jarvis, J. A. J.; Pearce, R.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1977**, 999. (b) van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1975**, *102*, 551. (c) Leusink, A. J.; van Koten, G.; Noltes, J. G. *J. Organomet. Chem.* **1973**, *56*, 379. (d) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1979**, *101*, 6593. (e) Bochmann, M.; Coleman, A. P.; Webb, K. J.; Hursthouse, M. B.; Mazid, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 973.

(9) Zhao, J.; Adcock, D.; Pennington, W.; Kolis, J. W. *Inorg. Chem.* **1990**, *29*, 4358.

(10) (a) McConnachie, J. M.; Ansari, M. A.; Bollinger, J. C.; Salm, R. J.; Ibers, J. A. *Inorg. Chem.*, **1993**, *32*, 3201. (b) Ansari, M. A.; Bollinger, J. C.; Ibers, J. A. *Inorg. Chem.* **1993**, *32*, 1746.

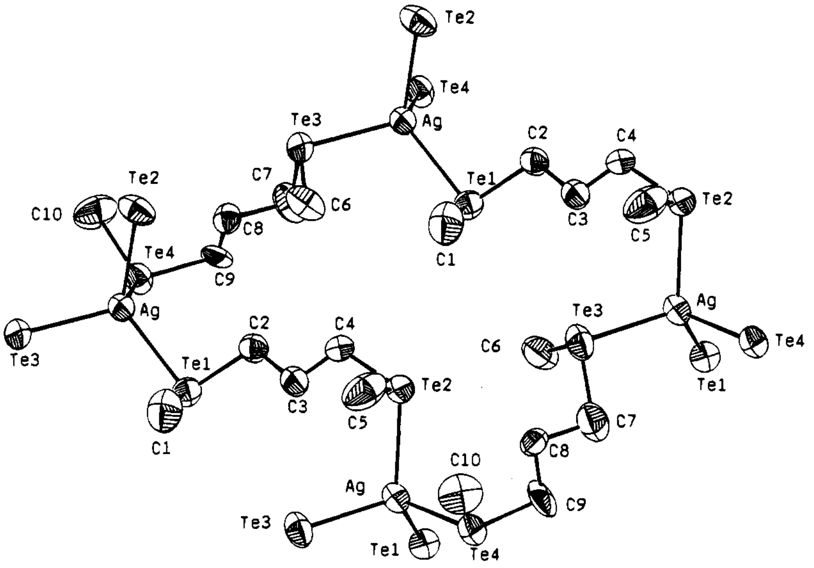

Figure 1. ORTEP drawing and labeling scheme of polymeric [Ag(MeTe(CH$_2$)$_3$TeMe)$_2$]$_n$ cation with thermal ellipsoids drawn at the 50% probability level.

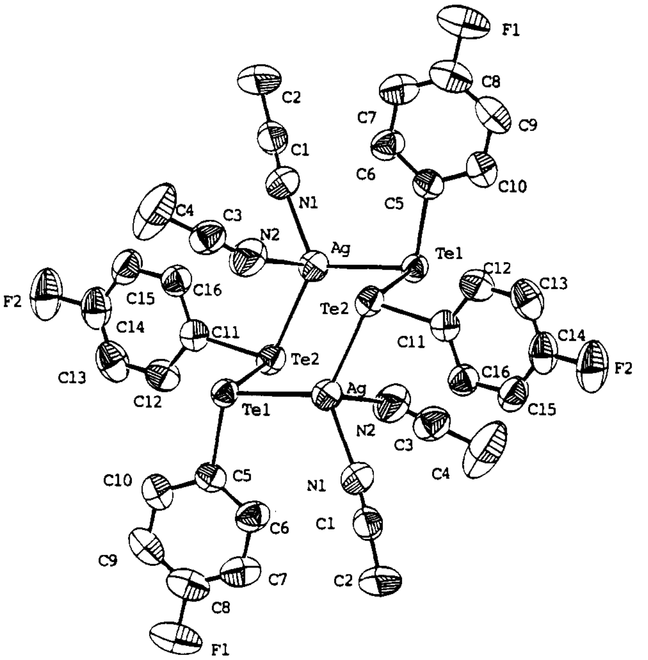

Figure 2. ORTEP drawing and labeling scheme of [Ag$_2$(NCCH$_3$)$_4$(μ_2-(p-C$_6$H$_4$F)TeTe(p-C$_6$H$_4$F))$_2$]$^{2+}$ with thermal ellipsoids drawn at the 50% probability level.

Structure of [Ag$_2$(NCCH$_3$)$_4$(μ_2-(p-C$_6$H$_4$F)TeTe(p-C$_6$H$_4$F))$_2$][BF$_4$]$_2$. The crystal structure of [Ag$_2$(NCCH$_3$)$_4$(μ_2-(p-C$_6$H$_4$F)TeTe(p-C$_6$H$_4$F))$_2$][BF$_4$]$_2$ was determined with X-ray diffraction (Figure 2). The silver cation Ag$^+$ and diorganyl ditelluride (Te(p-C$_6$H$_4$F))$_2$ exhibit an interesting mode of coordination. The two Ag(I) atoms are bridged by two bis(p-fluorophenyl) ditelluride ligands, and the six-membered Ag$_2$(TeTe)$_2$ ring adopts a chair configuration. The average Ag−Te distance 2.734(1) Å (Ag−Te(1) 2.736(1) Å and Ag−Te(2) 2.733(1) Å) in this complex differs from three other structurally characterized Ag−Te distances, shorter than the reported Ag−TeR bond 2.754(5) Å (average) in the [Ag$_4$(TeR)$_6$]$^{2-}$ (R = thienyl)[9] but longer than Ag−Te in the range 2.695(2)−2.725(2) Å in [AgTe$_7$]$^{2-}$ [10a] and 2.680(1)−2.710(1) Å in [(Te$_4$)Ag(μ-Te$_4$)Ag(Te$_4$)]$^{4-}$.[10b]

Of particular significance, the Te-Te bond of length 2.752(1) Å in this complex is longer than the Te−Te bond (2.712 Å) previously found in free diphenyl ditelluride PhTeTePh,[11] but is much shorter than the Te−Te bond of distances 2.794(5) and 2.901(3) Å found in Re$_2$(μ-Br)$_2$(μ-PhTeTePh)(CO)$_6$ and Ru$_2$(η^5-C$_5$Me$_5$)$_2$(μ-TeR)$_2$(μ-RTeTeR) (R = tol).[4] The bond angles Ag−Te(1)−Te(2) 92.65(2)°, Ag−Te(1)−C(5) 103.70(13)°, and Te(2)−Te(1)−C(5) 96.88(12)° indicate a greatly distorted tetrahedral disposition, with the fourth sp^3 orbital occupied by a lone pair of electrons about each tellurium atom. The coordination geometry around the Ag(I) center is also a distorted tetrahedron with an acute N(1)−Ag−N(2) angle 88.17(16)°, an Te(1)−Ag−Te(2) angle 120.49(3)°, and Te−Ag−N angles 116.58(12)°, 100.68(12)°, 119.07(12)°, and 100.47(12)°.

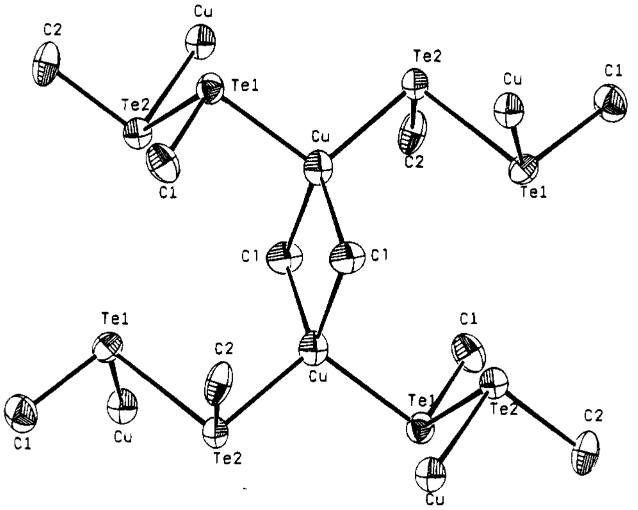

Figure 3. ORTEP drawing and labeling scheme of the polymeric [(μ_2-MeTeTeMe)Cu(μ-Cl)]$_n$ with thermal ellipsoids drawn at the 50% probability level.

Structure of [(μ_2-MeTeTeMe)Cu(μ-Cl)]$_n$. The [(μ_2-MeTeTeMe)Cu(μ-Cl)]$_n$ moieties are formed into a polymeric structure through linking Cu−(Me)TeTe(Me)−Cu bonds in the crystal (Figure 3). The core geometry of [(μ_2-MeTeTeMe)Cu(μ-Cl)]$_n$ moiety is best described as a Cu$_2$Cl$_2$ planar square. Each Cu(I) atom makes four bonds, two to tellurium atoms of two bimetallic μ_2-bridging MeTeTeMe ligands and two to two bridging chloride atoms. Two bimetallic μ_2-bridging MeTe-

---

[11] Llabres, G.; Dideberg, O.; Dupont, L. *Acta Crystallogr.* **1972**, *B28*, 2438.

TeMe groups and the bridging chloride ligands define the distorted tetrahedral geometry of each Cu(I) atom (angles Te(1)−Cu−Te(2) 107.17(6)°, Te(1)−Cu−Cl 115.7(1)°, Te(2)−Cu−Cl 119.7(1)°, Cl−Cu−Cl 90.9(1)°), leading to an acute bridge of Cu−Cl−Cu angle 89.1(1)°. As a consequence of MeTeTeMe bridging in the structure, the tellurium atoms of each MeTeTeMe ligand are equivalent.

The Cu(I)−Te bond of distance 2.547(2) Å (average) may be compared with Cu−Te distances in known solid-state compounds $[NEt_4]_4[Cu_2Te_{12}]$ (2.492(4)−2.514(4) Å)[12] and KCuTe (2.58(2) Å).[13,14] The Cu(I)−Cl bond length (average 2.408(3) Å) does in fact lie in the range 2.24−2.41 Å observed for terminal Cu−Cl bonds in other tetrahedral Cu(I) complexes.[15] The Cu(I)···Cu(I) distance 3.381(3) Å is much longer than the sum of van der Waals radii of Cu atoms (2.8 Å).[14] The length, 2.755(1) Å, of the Te(1)-Te(2) bond in $[(\mu_2\text{-MeTeTeMe})\text{Cu}(\mu\text{-Cl})]_n$ is comparable with another intact Te−Te distance, 2.752(1) Å, of the structurally characterized, corresponding cationic silver(I)−diorganyl ditelluride $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2]^{2+}$ reported here.

Conclusion. The ligand $MeTe(CH_2)_3TeMe$ exhibits diverse coordination patterns.[7bd,16] Here we report an X-ray-characterized ditelluroether coordination pattern missing from the list of previously identified monometallic bidentate ditelluroether and monometallic monoconnective telluroether.[7d] In this pattern two tellurium atoms of the $MeTe(CH_2)_3TeMe$ chain participate in the formation of polymeric species $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$.

A new homo-diorganyl ditelluride doubly-bridged complex $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$ was prepared. This work provides an example of a metal−tellurium complex having two RTe−TeR ($R = p\text{-}C_6H_4F$) units bridging two metal atoms and may provide additional insight into the cleavage of the Te−Te bond of diorganyl ditellurides during nucleophilic or electrophilic reactions.

Experimental Section

Manipulations, transfers, and reactions of samples were conducted under nitrogen with standard Schlenk techniques or in a glovebox. Solvents were distilled under nitrogen from appropriate drying agents (acetonitrile and diethyl ether from CaH_2; hexane and tetrahydrofuran-(THF) from Na/benzophenone) and then stored in dried, N_2-filled flasks over activated 4 Å molecular sieves. A nitrogen purge was used on these solvents prior to use and transfers to reaction vessels were via stainless steel cannula under a positive pressure of N_2. The reagents silver tetrafluoborate, copper(I) chloride, tellurium powder, methyllithium, phenylmagnesium bromide, and 1,3-dibromopropane (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-7 FTIR) using sealed solution cells (0.1 mm) with KBr windows. NMR spectra were recorded on a Bruker AC 200 spectrometer; chemical shifts for ^1H and ^{13}C NMR spectra are relative to tetramethylsilane; chemical shifts for ^{125}Te NMR spectra are relative to Me_2Te (298 °C). Analyses of carbon and hydrogen were obtained with a CHN analyzer (Heraeus).

Table 1. Crystallographic Data for $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ (**1**), $[Ag_2(NCCH_3)_4(\mu\text{-}((p\text{-}C_6H_4F)Te)_2)_2][BF_4]_2$ (**2**), and $[(\mu\text{-MeTeTeMe})\text{Cu}(\mu\text{-Cl})]_n$ (**3**)

	1	**2**	**3**
chem formula	$AgTe_4C_{10}H_{24}BF_4$	$Ag_2Te_4C_{32}N_4H_{28}B_2F_{12}$	$Cu_2Te_4Cl_2C_4H_{12}$
fw	849.36	1416.10	768.53
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
λ, Å (Mo Kα)	0.70930	0.70930	0.70930
a, Å	8.755(3)	6.835(2)	9.923(2)
b, Å	20.441(8)	13.255(2)	8.091(2)
c, Å	12.227(3)	13.842(4)	10.232(3)
α, deg	90	116.48(3)	90
β, deg	103.13(3)	95.95(2)	116.01(2)
γ, deg	90	98.90(2)	90
V, Å^3	2130.9(12)	1086.2(4)	738.3(3)
Z	4	1	2
ϱ_{calcd}, g cm^{-3}	2.648	2.165	3.457
μ, cm^{-1}	63.452	36.128	109.937
T, °C	25	25	25
R^a	0.057	0.027	0.027
$R_w{}^b$	0.062	0.028	0.025

[a] $R = \sum|F_o - F_c|/F_o$. [b] $R_w = [\sum(w(F_o - F_c)^2/wF_o{}^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$

Ag−Te(1)	2.789(2)	Te(1)−C(1)	2.07(3)
Ag−Te(2)	2.820(2)	Te(1)−C(2)	2.15(2)
Ag−Te(3)	2.785(2)	Te(2)−C(4)	2.14(2)
Ag−Te(4)	2.837(2)	Te(2)−C(5)	2.09(4)
Te(1)−Ag−Te(2)	122.51(8)	Ag−Te(1)−C(1)	99.2(8)
Te(1)−Ag−Te(3)	111.55(7)	Ag−Te(1)−C(2)	97.1(6)
Te(1)−Ag−Te(4)	104.96(7)	C(1)−Te(1)−C(2)	94.8(10)
Te(2)−Ag−Te(3)	106.53(8)	C(2)−C(3)−C(4)	110.0(17)
Te(2)−Ag−Te(4)	99.48(7)	Te(1)−C(2)−C(3)	113.0(14)
Te(3)−Ag−Te(4)	110.94(8)		

Synthesis of $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$. $AgBF_4$ (0.1 g, 0.5 mmol) was loaded into a Schlenk flask (20 mL) and dissolved in CH_3CN (5 mL) in a dark environment at ambient temperature. $MeTe(CH_2)_3TeMe$ (2 mL, 0.5 M in THF)[7a, 16] was syringed into the $AgBF_4$−acetonitrile solution. The reaction mixture was stirred for 10 min, and diethyl ether was added to precipitate the orange-yellow solid; then the solvent was removed via cannula. Recrystallization by dissolving the product in CH_3CN, layering it with diethyl ether, and keeping it in the refrigerator at −10 °C for 3 weeks afforded light orange-yellow crystals $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ (0.241 g, 92%). ^1H NMR (CD_3CN): δ 2.08 (s) (Me, $J_{^1H-^{125}Te}$ = 17.6 Hz, satellite), 2.82 (t) ($TeCH_2$-), 2.20 (q) ppm ($TeCH_2CH_2$-). ^{13}C NMR (CD_3CN): −15.52 (s), 8.93 (s), 29.17 (s) ppm. ^{125}Te NMR (CD_3CN): 24.4 (s) ppm.

Synthesis of $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$. A solution of $AgBF_4$ (97 mg, 0.5 mmol) in acetonitrile (5 mL) was stirred with $(Te(p\text{-}C_6H_4F))_2$ (224 mg, 0.5 mmol)[16a,b] for 0.5 h at room temperature, resulting in the formation of a blood-red solution. The reaction mixture was concentrated to 3 mL, and diethyl ether was slowly added to precipitate a red solid. The mother liquor was removed via cannula, and the solid was dried under vaccum. The light-sensitive red solid was isolated in 96% (0.334 g) yield. Recrystallization on dissolving the red solid in a minimum amount of CH_3CN, layering it with diethyl ether (5-fold proportion), and then cooling to −10 °C for 2 weeks afforded blood-red crystals of $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$. ^1H NMR (CD_3COCD_3): δ 2.05 (s) (CH_3CN), 7.07−7.16 (m), 7.92−8.00 (m) (C_6H_4F). ^{13}C NMR (CD_3COCD_3): 117.66, 1.07 ppm (CH_3CN), 166.79, 163.52, 141.87, 141.73, 118.08 ppm (C_6H_4F). ^{125}Te NMR (CD_3CN): 455.1 ppm (s). IR $\nu_{(C\equiv N)}$ (THF) 2050 (br) cm^{-1}. Anal. Calcd for $Ag_2Te_4C_{32}N_4H_{28}B_2F_{12}$: N, 3.96; C, 27.14; H, 1.99. Found: N, 3.93; C, 26.54; H, 1.98.

Synthesis of $[(\mu_2\text{-MeTeTeMe})\text{Cu}(\mu\text{-Cl})]_n$. Into a 20 mL Schlenk flask were charged CuCl (0.04 g, 0.4 mmol) and a portion of MeTeTeMe (0.92 mL, 0.4326 M in THF)[16] in CH_3CN (5 mL) at ambient temperature. The reaction mixture was stirred for 10 min, and diethyl ether was added to precipitate the red-brown solid. Upon removal of the mother liquor via cannula, a red-brown solid $[(\mu_2\text{-MeTeTeMe})\text{Cu}(\mu\text{-Cl})]_n$ (0.13 g, 85%) was obtained.[6] Recrystallization of the product from a minimum volume of CH_3CN, layering it with

---

(12) Ansari, M. A.; Bollinger, J. C.; Ibers, J. A. *Inorg. Chem.* **1993**, *32*, 1746.

(13) Savelsberg, G.; Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33*, 370.

(14) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 5871.

(15) (a) Girling, R. L.; Amma, E. L. *Inorg. Chem.* **1971**, *10*, 335. (b) Cotton, F. A.; Frenz, B. A.; Hunter, D. L.; Mester, Z. C. *Inorg. Chim. Acta* **1974**, *11*, 111.

(16) (a) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97. (b) Irgolic, K. J.; Busse, P. J.; Grigsby, R. A.; Smith, M. R. *J. Organomet. Chem.* **1975**, *88*, 175. (c) Hope, E. G.; Kemmitt, T.; Levason, W. *Organometallics* **1988**, *7*, 78. (d) Pathirana, H. M. K. K.; McWhinnie, W. R. *J. Chem. Soc., Dalton Trans.* **1988**, 2003.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$

Ag−Te(1)	2.736(1)	Ag−N(2)	2.573(5)
Ag−Te(2)	2.733(1)	Te(1)−Te(2)	2.752(1)
Ag−N(1)	2.253(4)	Te(1)−C(5)	2.126(5)
Te(1)−Ag−Te(2)	120.49(3)	Ag−Te(2)−Te(1)	90.97(3)
Te(1)−Ag−N(1)	116.58(12)	Ag−Te(1)−C(5)	103.70(13)
Te(1)−Ag−N(2)	100.68(12)	Ag−Te(2)−C(11)	105.64(13)
Te(2)−Ag−N(1)	119.07(12)	Ag−N(1)−C(1)	167.4(4)
Te(2)−Ag−N(2)	100.47(12)	Ag−N(2)−C(3)	125.7(5)
N(1)−Ag−N(2)	88.17(16)	N(1)−C(1)−C(2)	178.8(6)
Ag−Te(1)−Te(2)	92.65(2)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$

Cu−Te(1)	2.565(2)	Te(1)−Te(2)	2.755(1)
Cu−Te(2)	2.529(2)	Te(1)−C(1)	2.118(11)
Cu−Cl	2.336(3)	Te(2)−C(2)	2.151(12)
Cu−Cl	2.479(3)	Cu••Cu	3.381(3)
Te(1)−Cu−Te(2)	107.17(6)	Cl−Cu−Cl	90.87(11)
Te(1)−Cu−Cl	115.74(10)	Cu−Te(1)−Te(2)	90.60(5)
Te(1)−Cu−Cl	111.20(10)	Cu−Cl−Cu	89.13(11)
Te(2)−Cu−Cl	119.71(10)	Cu−Te(1)−C(1)	96.4(3)
Te(2)−Cu−Cl	111.18(9)	Te(2)−Te(1)−C(1)	96.7(3)

Table 5. Fractional Atomic Coordinates and B_{eq} Values (Å^2) of $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$[a]

	x	y	z	B_{eq}[b]
Ag	0.70000(18)	0.89953(8)	0.21632(14)	4.48(7)
Te1	0.61879(18)	0.82204(7)	0.02412(12)	4.68(7)
Te2	0.58009(19)	0.87702(9)	0.40846(14)	6.15(9)
Te3	1.02411(17)	0.91047(9)	0.29097(14)	5.95(8)
Te4	0.56208(17)	1.02321(7)	0.15100(13)	4.70(7)
C1	0.742(4)	0.7382(15)	0.084(3)	8.5(17)
C2	0.3988(24)	0.7871(10)	0.0513(19)	4.9(10)
C3	0.3376(24)	0.7266(11)	−0.0194(19)	5.0(11)
C4	0.685(3)	0.7942(12)	0.5028(18)	5.4(11)
C5	0.725(4)	0.9461(15)	0.5071(23)	9.4(20)
C6	1.104(3)	0.8178(13)	0.2471(24)	7.2(16)
C7	1.078(3)	0.9590(13)	0.154(3)	7.2(16)
C8	1.273(5)	0.9672(21)	0.199(3)	4.5(20)
C9	0.319(5)	1.005(3)	0.106(4)	7.5(31)
C8′	1.234(5)	0.9619(23)	0.116(4)	6.2(24)
C9′	0.328(5)	1.0102(20)	0.183(5)	6.6(30)
C10	0.599(4)	1.0870(13)	0.2896(24)	8.2(17)
B	0.00364	0.14583	0.18922	15.79
F1	0.15434	0.13664	0.23621	15.79
F2	0.02831	0.14915	0.06955	15.79
F3	−0.03921	0.21017	0.20717	15.79
F4	0.01797	0.10014	0.26732	15.79

[a] Esd's refer to the last digit printed [b] $B_{eq} = {}^8/_3\pi^2\Sigma_i\Sigma_jU_{ij}a_i{}^*a_j{}^*a_ia_j$.

diethyl ether, and then cooling to −10 °C for 4 weeks afforded red-brown crystals of $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$. ^1H NMR (CD_3CN): δ 2.63 (s) (satellite, $J_{^1H-^{125}Te} = 23.2$ Hz). ^{13}C NMR (CD_3CN): δ −20.51-(s) ppm. ^{125}Te NMR (CD_3CN): 30.0 (s) ppm. Anal. Calcd for $C_4H_{12}Cl_2Te_4Cu_2$: C, 6.26; H, 1.57. Found: C, 6.37; H, 1.35.

Table 6. Fractional Atomic Coordinates and B_{eq} Values (Å^2) of $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$[a]

	x	y	z	B_{eq}[b]
Ag	0.27452(6)	0.06486(3)	0.09525(3)	5.124(21)
Te1	0.07924(5)	−0.12690(3)	0.10319(3)	3.894(15)
Te2	0.28524(5)	0.06316(3)	−0.10256(3)	4.146(16)
N1	0.5141(7)	0.1920(4)	0.2430(3)	5.9(3)
N2	0.0342(8)	0.2008(4)	0.1700(4)	7.4(3)
C1	0.6102(8)	0.2496(4)	0.3265(4)	5.2(3)
C2	0.7365(11)	0.3220(6)	0.4326(5)	9.4(5)
C3	0.0779(8)	0.2946(5)	0.2159(4)	5.9(3)
C4	0.1325(13)	0.4174(6)	0.2745(8)	13.1(7)
C5	0.1437(7)	−0.0810(4)	0.2733(4)	4.2(3)
C6	0.2252(7)	0.0305(4)	0.3528(4)	5.1(3)
C7	0.2682(8)	0.0553(5)	0.4627(4)	5.9(3)
C8	0.2275(8)	−0.0321(5)	0.4865(4)	6.1(4)
C9	0.1428(9)	−0.1437(5)	0.4095(5)	6.4(4)
C10	0.0998(8)	−0.1684(5)	0.3015(4)	5.5(3)
C11	0.4655(6)	0.2268(4)	−0.0642(4)	4.1(3)
C12	0.4881(8)	0.2511(5)	−0.1499(4)	5.1(3)
C13	0.6048(8)	0.3572(5)	−0.1287(5)	6.2(4)
C14	0.6935(7)	0.4337(4)	−0.0231(5)	5.8(3)
C15	0.6743(8)	0.4128(4)	0.0637(5)	5.5(3)
C16	0.5569(7)	0.3075(4)	0.0434(4)	4.7(3)
F1	0.2696(6)	−0.0095(4)	0.5940(3)	8.9(3)
F2	0.8059(5)	0.5379(3)	−0.0019(3)	8.5(3)
B	0.6996(13)	0.5993(7)	0.3898(7)	8.5(6)
F3	0.8539(8)	0.6182(5)	0.3443(5)	16.4(5)
F4	0.5588(8)	0.6493(4)	0.3679(4)	13.5(4)
F5	0.7635(9)	0.6475(6)	0.4937(4)	17.4(6)
F6	0.6250(8)	0.4864(4)	0.3353(5)	15.4(5)

[a] Esd's refer to the last digit printed. [b] $B_{eq} = {}^8/_3\,\pi^2\,\Sigma_i\Sigma_j\,U_{ij}a_i{}^*a_j{}^*a_ia_j$.

Table 7. Fractional Atomic Coordinates and B_{eq} Values (Å^2) of $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$[a]

	x	y	z	B_{eq}[b]
Cu	0.47282(16)	0.02083(19)	0.32578(16)	2.87(8)
Te1	0.75100(9)	−0.32925(10)	0.37294(9)	2.48(4)
Te2	0.65960(9)	−0.03500(10)	0.22453(9)	2.38(4)
Cl	0.4132(3)	−0.1885(4)	0.4489(3)	3.13(17)
C1	0.9087(13)	−0.3922(16)	0.2934(14)	3.7(8)
C2	0.8269(12)	0.1182(15)	0.3865(13)	3.2(7)

[a] Esd's refer to the last digit printed. [b] $B_{eq} = {}^8/_3\,\pi^2\,\Sigma_i\,\Sigma_j\,U_{ij}a_i{}^*a_j{}^*a_ia_j$.

Crystallography. The crystal data are summarized in Table 1. The extremely light-sensitive crystal $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ chosen for diffraction measurement was ca. 0.10 × 0.30 × 0.40 mm (the red-brown crystal $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$ had crystal dimensions 0.05 × 0.05 × 0.40 mm and the light-sensitive crystal $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$ had crystal size 0.05 × 0.25 × 0.45 mm) and was mounted on a glass fiber and quickly coated in epoxy resin. The unit-cell parameters were obtained from 25 reflections with 2θ between 14.76° and 21.78° for $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$ ($16.16° < 2\theta < 20.18°$ for $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$; $18.68° < 2\theta < 34.0°$ for $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$). Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation employing the $\theta/2\theta$ scan mode. Structural determinations were made using the NRCC-SDP-VAX package of programs.[17] In the structure of $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$, the $\text{-}CH_2CH_2CH_2\text{-}$ chain ligands have apparent disorder. The minimized function was $\Sigma w(|F_o| - |F_c|)^2$, in which w ($= 1/\sigma^2(F_o)$) is the weight of a given observation. Selected bond distances and angles are listed in Tables 2−4. Fractional atomic coordinates and B_{eq} values (Å^2) are listed in Tables 5−7.

Acknowledgment. We thank the National Science Council of the Republic of China (Taiwan) for support of this work.

Supporting Information Available: Tables of crystal data and experimental conditions for the X-ray studies, bond lengths and angles, anisotropic temperature factors for $[Ag(MeTe(CH_2)_3TeMe)_2]_n[BF_4]_n$, $[(\mu_2\text{-}MeTeTeMe)Cu(\mu\text{-}Cl)]_n$, $[Ag_2(NCCH_3)_4(\mu_2\text{-}(p\text{-}C_6H_4F)TeTe(p\text{-}C_6H_4F))_2][BF_4]_2$ (13 pages). Ordering information is given on any current masthead page.

IC941088I

---

[17] Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.