# Synthesis and Characterization of Functionalized *N,N′*-Diphenylformamidinate Silver(I) Dimers: Solid-State Structures and Solution Properties

**Stephen J. Archibald,‡ Nathaniel W. Alcock,† Daryle H. Busch,*,‡ and David R. Whitcomb§**

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom, and Dry Media Systems Laboratory, Imation Corporation, St. Paul, Minnesota 55144

Functionalized *N,N′*-diphenylformamidines and their deprotonated silver(I) complexes have been synthesized: silver(I) *N,N′*-di(4-alkyl)phenylformamidinate (alkyl = methyl, ethyl, *n*-butyl, and *n*-hexadecyl) **1**−**4**; silver(I) *N,N′*-di(4-trifluoromethyl)phenylformamidinate **5**, silver(I) *N,N′*-di(3-methoxy)phenylformamidinate **6**, silver(I) *N,N′*-di(3-methylmercapto)phenylformamidinate **7**, silver(I) *N,N′*-di(2-methoxy)phenylformamidinate **8**, silver(I) *N,N′*-di(2-methylmercapto)phenylformamidinate **9**. The effects of increasing the coordination number of the silver(I) centers by donor substituents on the phenyl groups have been investigated by solution and solid-state studies. Variable-temperature proton NMR (223−303 K) for **1**−**4** shows coupling between the proton attached to the amidinate carbon and the $^{107/109}$Ag centers at room temperature which is unaffected by cooling (**2**). For the four-coordinate complexes, **8** and **9**, such coupling is only observed on cooling. Molecular weight measurements recorded in solution by vapor pressure osmometry at 310 K show some aggregation to higher molecular weight species than simple dimers for **1**−**4** and **6**, but **8** and **9** exist as discrete dimeric species. Measurement of thermal stability shows the expected increase in stability with increasing coordination number. Compounds **8** and **9** were structurally characterized by X-ray methods. Both show four-coordinate silver dimers bridged by two amidinate ligands with additional longer interactions with the ether oxygens or thioether sulfurs.

## Introduction

Amidinate and triazenate anions, isoelectronic with carboxylate, have been shown to act as bridging ligands with closed-shell Group 11 ions.[1] The structures observed for such triazenates and amidinates can be generalized in terms of the motifs shown in Figure 1, in which the difunctional ligands bridge pairs of ions. The resulting aggregates most commonly contain either dimers or tetramers (*n* = 1 or 2).

Silver carboxylates have been extensively investigated over the last 15 years with a large number of structures published, identifying the favored structural types.[2−6] More recent work on triazenate, amidinate, and guanidinate transition metal
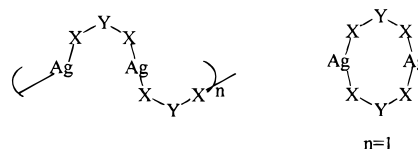


**Figure 1.** Subunits in silver(I) amidinate, triazenate, and some carboxylate structures.

complexes has identified their common structural types and revealed their potential for considerable variation in steric and electronic properties.[7] Suitable systems may display novel catalytic properties[8] and these ligands can stabilize unusual combinations of oxidation states in their dimeric complexes.[9]

† University of Warwick.
‡ University of Kansas.
§ Imation Corp.
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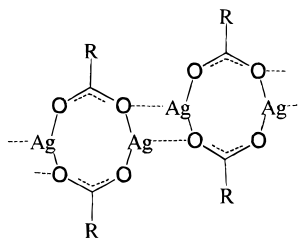
**Figure 2.** Polymeric unit common in silver(I) carboxylate structures.

Silver carboxylates have found uses in industrial processes and organic synthesis, creating interest in related compounds whose properties might be very different. Of particular importance is the ability to tune the stability of the compounds. This offers potential improvements in current processes and creates the possibility for novel applications.[10]

Silver(I) carboxylates show a number of solid-state structural configurations and coordination numbers, most commonly based on eight-membered rings formed from *O,O'*-bridged dimers, bis-(carboxylato)disilver(I) (Figure 1, X = O, Y = CCH₃, n = 1). Silver carboxylates frequently also form step polymeric arrays by the bridging of neighboring dimeric units with longer range O−Ag bonds, as shown in Figure 2. Few discrete dimeric structures[4] have been observed (silver coordination number of 2) and coordination numbers in the range 3−5 are more numerous. Polymeric chains, as opposed to linked dimers, have also been observed, e.g., silver(I) (4-chloro-2-methylphenoxy)-acetate.[5] However, this structure type is rare.

Previous studies on amidinate/triazenate complexes with d¹⁰ metal ions have focused on their structures and on the potential for metal−metal bonding in their dimers. Structural determinations of amidinate and triazenate complexes with copper(I), silver(I), and gold(I) have only found two-coordinate metal centers. Two structural motifs are normal, the dimer (n = 1)[11−15] and the tetramer (n = 2),[16−18] with one polymeric example reported.[11] The factors controlling which structure is formed are unclear; however, it has been postulated that the steric demands of an alkyl substituent on the amidinate carbon in a silver(I) *N,N'*-diphenylamidinate may favor tetramer formation in the solid state. The dimeric structure of one silver(I) *N,N'*-diarylformamidinate has been determined by X-ray diffraction [bis(*N,N'*-di-*p*-tolylformamidinato)silver(I), **1**].[14]

The principal interest in these structures has been in the silver−silver distances and the possibility of a bonding interaction between the d¹⁰ metal centers involving s- or p-orbitals. Cotton et al.[14] concluded that there was no evidence for such an interaction in bis(*N,N'*-di-*p*-tolylformamidinato)silver(I), despite the relatively short Ag−Ag distance of 2.705 Å. More compelling evidence for metal−metal bonding would come from close contacts unsupported by bridging ligands. Experimentally,

few such examples have been identified,[19] although work on polymetallic d¹⁰ complexes of gold[20] and platinum[21] has suggested metal−metal bond formation. In the case of copper-(I) the existence of such an interaction has been the source of debate with calculations at various theoretical levels providing support for both opposing views.[22,23] The recent publication of a structure with an unsupported copper(I)−copper(I) distance of 2.810(2) Å[19c] suggests that bonding interactions are indeed real.

Against this background, we felt it would be of interest to synthesize dimeric silver amidinate complexes with coordination numbers greater than 2. We postulated that the introduction of further coordinating groups would increase the stability of the dimers toward thermal decomposition, as has been found with the polymeric silver carboxylates, thereby broadening the range of their potential applications. This strategy has been implemented by the synthesis of substituted *N,N'*-diphenylforma-midinate complexes, which are more stable than the *N*-alkyl compounds.[24] Incorporation of functional groups capable of coordinating to a metal ion at the 2-position on the phenyl rings provides additional coordinating groups for the silver ions. For comparison *N,N'*-diphenylformamidinate ligands were synthe-sized with the same substituents in the 3-position on the phenyl rings, and their silver complexes were also prepared. Further, preparation of a number of 4-alkyl-substituted ligands and their complexes made it possible to contrast the properties of two- and four-coordinate silver(I) amidinate dimers. Thermal stabili-ties have been investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and solution properties by variable-temperature proton NMR and molecular mass measurements. Crystal structures have been obtained for two four-coordinate species.

## Experimental Section

**Materials and Methods.** All reagents were purchased from the Aldrich Chemical Co., with the exception of silver nitrate, which was supplied by the Ames Goldsmith Corp.; all were used without further purification. Infrared spectra were obtained from KBr pressed disks on a Perkin-Elmer Model 1600 Fourier transform spectrometer. NMR spectra were collected on General Electric QE-300, Bruker DRX-400, and Bruker AM-500 spectrometers and referenced to signals from residual solvent protons. Variable-temperature proton NMR spectra were recorded on the Bruker AM-500 spectrometer with a standard Bruker temperature control unit having an accuracy of ±1 °C. Fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB MS mass spectrometer equipped with a xenon gun and 3-nitrobenzyl alcohol (3-NBA) as the matrix material. DSC was carried out under N₂ purge, 25 mL/min, heating at 10 °C/min on a 9900 TA Instruments thermal analyzer with dual sample cell, model 912 DSC, calibrated with 99.99% indium. TGA was carried out under the same conditions on the TA Instruments model 951 TGA analyzer. Molecular mass measurements were carried out on solutions in chloroform at concentrations of 0.01− 0.03 M with a Hewlett-Packard model 302 vapor pressure osmometer operating at 37 °C. Calibration was performed with benzil standards

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**Table 1.** Crystallographic Data for **8** and **9**

| | 8 | 9 |
|---|---|---|
| formula | $C_{30}H_{30}N_4O_4Ag_2$ | $C_{30}H_{30}N_4S_4Ag_2$ |
| formula weight | 726.32 | 790.56 |
| crystal system | orthorhombic | monoclinic |
| space group | $Pca2_1$ | $P2_1$ |
| $a$, Å | 24.7386(3) | 8.0228(1) |
| $b$, Å | 11.3363(1) | 14.4933(3) |
| $c$, Å | 10.3987(1) | 13.3917(2) |
| $\beta$, deg | 90 | 106.724(1) |
| $U$, Å$^3$ | 2916.26(5) | 1491.28(4) |
| $T$, K | 180(2) | 180(2) |
| Z | 4 | 2 |
| $d_{calcd}$, g/cm$^3$ | 1.654 | 1.761 |
| crystal size, mm | $0.32 \times 0.22 \times 0.19$ | $0.21 \times 0.20 \times 0.04$ |
| $\mu$ (Mo K$\alpha$), mm$^{-1}$ | 1.384 | 1.621 |
| unique data | 6761 | 6458 |
| total data | 17576 | 9218 |
| data [$I > 2\sigma(I)$] | 5743 | 5051 |
| parameters | 368 | 366 |
| R1, wR2 | 0.0488, 0.0909 | 0.0341, 0.0613 |
| weighting scheme, w$^{-1}$ | $\sigma^2(F_o^2) + (0.01P)^2 + 8P$ | $\sigma^2(F_o^2) + (0.0153P)^2$ |
| goodness of fit | 1.165 | 0.922 |
| largest residuals, e·Å$^{-3}$ | 0.462, −0.515 | 0.593, −1.073 |

and multiple readings were taken for each data point. Errors in mass measurements are expected to be of the order ± 5%.

**Crystal Stucture Analysis: Data Collection and Processing.** Colorless blocks of **8** were grown by diffusion of ether vapor into a concentrated dichloromethane solution of the complex at −4 °C. Colorless plates of **9** were produced by diffusion of methanol vapor into a 1,2-dichloroethane solution at 4 °C. Crystallographic data were collected on a Siemens SMART three-circle diffractometer with a CCD area detector.[25] An absorption correction by $\psi$-scan was applied for **9** (transmission range 0.69−0.93) but was found to be unnecessary for **8**. Neither crystal showed decay during data collection. Details of the crystal parameters, data, cell, and refinement are in Table 1. Systematic absences indicated space groups $Pca2_1$ or Pcam for **8** and $P2_1$ or $P2_1/m$ for **9**. In both cases, the centrosymmetric (second) alternative would have required molecular symmetry that was unlikely to be present. The noncentrosymmetric alternatives were chosen and confirmed by successful refinement.

**Structure Analysis and Refinement.** Both structures were solved by direct methods by use of SHELXS (TREF)[26] with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined by use of a riding model with freely rotating methyl groups. For **8**, two of the methyl groups had alternative positions at about 50% occupancy [0.50(5) for C19A and 0.58(4) for C29A]; the O−C (methyl) distances were restrained to be equal at 1.458(2) Å. For both **8** and **9**, the absolute structures were confirmed by refinement of a $\delta f''$ multiplier, but **9** proved to be an inversion twin [fraction of second component 0.26(2)]. Floating origin constraints were generated automatically. Anisotropic displacement factors were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached. Refinement used SHELXL 96.[26] Selected bond lengths and angles for **8** and **9** are given in the captions to Figures 4 and 5, respectively.

**Amidine Ligand Synthesis.** All amidine ligands were synthesized by modified literature procedures.[27−29] In the preparations, the reaction

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time, temperature, and the method of recrystallization varied from case to case. General procedure: The ortho ester (0.1 mol) and the aniline derivative (0.2 mol) were mixed and acetic acid (0.5−1.0 mL) was added. The reaction mixture was heated to between 140 and 160 °C for a period of 3−4 h and then distilled at the reaction temperature to remove the ethanol that formed and give the desired product. The viscous reaction mixture was cooled to ambient temperature, whereupon it solidified. This solid was extracted with warming into petroleum ether/benzene. The solution was cooled in the freezer and concentrated, if necessary, to give white crystalline solids in yields of 50−80%. Amidines were characterized by $^1$H and $^{13}$C NMR, elemental analysis, and mass spectroscopy.

***N,N′*-Di-*p*-tolylformamidine.** Elemental analysis: observed, C, 80.1; H, 6.89; N, 12.9. $C_{15}H_{16}N_2$ requires C, 80.3; H, 7.19; N 12.5. $^1$H NMR (CDCl$_3$): $\delta$ 2.12 (s, 6 H, CH$_3$), 6.83 (d, 4 H, CH phenyl), 7.00 (d, 4 H, CH phenyl), 8.07 (s, 1 H, CH amidine). $^{13}$C NMR: $\delta$ 21.2 (CH$_3$), 119.5 (phenyl), 130.3 (phenyl), 133.1 (phenyl), 143.2 (phenyl), and 150.9 (amidine C). MS (EI): *m/z* 223 [M]$^+$.

***N,N′*-Di(4-ethyl)phenylformamidine.** Elemental analysis: observed, C, 79.7; H, 8.18; N, 10.4. $C_{17}H_{20}N_2$·0.3H$_2$O requires C, 79.2; H, 8.06; N 10.9. $^1$H NMR (CDCl$_3$): $\delta$1.13 (t, 6 H, CH$_3$), 2.54 (quartet, 4 H, CH$_2$), 6.87 (d, 4 H, CH phenyl), 7.03 (d, 4 H, CH phenyl), 8.09 (s, 1 H, CH amidine). $^{13}$C NMR: $\delta$ 16.2, 28.6, 119.5, 129.1, 139.7, 143.2, and 149.7. MS (EI): *m/z* 251 [M]$^+$.

***N,N′*-Di(4-butyl)phenylformamidine.** Elemental analysis: observed, C, 80.0; H, 8.49; N, 8.50. $C_{21}H_{28}N_2$·0.5EtOH requires C, 80.4; H, 8.59; N, 8.53. $^1$H NMR (CDCl$_3$): $\delta$ 0.85 (t, 6 H, CH$_3$), 1.27 (m, 4 H, CH$_2$), 1.49 (quintet, 4 H, CH$_2$), 2.48 (t, 4 H, CH$_2$), 6.83 (d, 4 H, CH phenyl), 7.01 (d, 4 H, CH phenyl), 8.08 (s, 1 H, CH amidine). $^{13}$C NMR: $\delta$ 14.4, 22.8, 34.2, 35.4, 119.4, 129.7, 138.2, 143.4, and 150.0. MS (EI): *m/z* 308 [M]$^+$.

***N,N′*-Di(4-hexadecyl)phenylformamidine.** Elemental analysis: observed, C, 81.3; H, 13.0; N, 3.89. $C_{45}H_{76}N_2$·EtOH requires C, 81.7; H, 11.9; N 4.05. $^1$H NMR (CDCl$_3$): $\delta$ 0.81 (t, 6 H, CH$_3$), 1.25 (br s, 52 H, CH$_2$), 1.51 (br s, 4 H, CH$_2$), 2.51 (t, 4 H, CH$_2$), 7.01 (d, 4 H, CH phenyl), 7.10 (d, 4 H, CH phenyl), 8.13 (s, 1 H, CH amidine). $^{13}$C NMR: $\delta$ 14.5, 23.1, 29.7, 29.8, 29.9, 30.0, 30.1, 31.9, 32.3, 35.7, 118.9, 130.0, 138.0, 140.4, and 149. MS (EI): *m/z* 643 [M]$^+$.

***N,N′*-Di(4-trifluoromethyl)phenylformamidine.** Elemental analysis: observed, C, 54.1; H, 2.98; N, 8.05. $C_{15}H_{10}N_2F_6$ requires C, 54.2; H, 3.03; N, 8.43. $^1$H NMR (CDCl$_3$): $\delta$ 7.0 (d, 4 H, CH phenyl), 7.50 (d, 4 H, CH phenyl), 8.20 (s, 1 H, CH amidine). MS (EI): *m/z* 332 [M]$^+$, 172 [CNPhCF$_3$]$^+$, 161 [NHPhCF$_3$]$^+$.

***N,N′*-Di(3-methoxy)phenylformamidine.** Elemental analysis: observed, C, 70.23; H, 6.20; N, 11.2. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.29; N, 10.9. $^1$H NMR (CDCl$_3$): $\delta$ 3.56 (s, 6 H, −OCH$_3$), 6.4−6.6 (overlap, 6 H, CH phenyl), 7.09 (dd, 4 H, CH phenyl), 8.16 (s, 1 H, CH amidine). $^{13}$C NMR: $\delta$ 55.5, 105.4, 109.9, 111.5, 130.6, 147.1, 150.5, and 161.1. MS (EI): *m/z* 256 [M]$^+$.

***N,N′*-Di(3-methylmercapto)phenylformamidine.** Elemental analysis: observed, C, 62.2; H, 5.68; N, 9.80. $C_{15}H_{16}N_2S_2$ requires C, 62.5; H, 5.59; N, 9.71. $^1$H NMR (CDCl$_3$): $\delta$ 2.33 (s, 6 H, −SCH$_3$), 5.77 (v br s, 1 H, NH), 6.72 (d, 2 H, CH phenyl), 6.81(s, 2 H, CH phenyl), 6.90 (d, 2 H, CH phenyl), 7.14 (dd, 2 H, CH phenyl), 8.11 (s, 1 H, CH amidine). MS (EI): *m/z* 287 [M]$^+$, 150 [M − NHPhSMe]$^+$, 139 [NHPhSMe]$^+$.

***N,N′*-Di(2-methoxy)phenylformamidine.** Elemental analysis: observed, C, 70.1; H, 6.21; N, 10.7. $C_{15}H_{16}N_2O_2$ requires C, 70.3; H, 6.29; N, 10.9. $^1$H NMR (CDCl$_3$): $\delta$ 3.83 (s, 6 H, −OCH$_3$), 6.8−7.15 (overlap br s, 8 H, CH phenyl), 8.22 (s, 1 H, CH amidine). $^{13}$C NMR: $\delta$ 56.1, 111.5, 117.8, 121.6, 123.8, 148.0, and 152.1. MS (EI): *m/z* 255 [M]$^+$.

***N,N′*-Di(2-methylmercapto)phenylformamidine.** Elemental analysis: observed, C, 62.1; H, 5.40; N, 9.68. $C_{15}H_{16}N_2S_2$ requires C, 62.5; H, 5.59; N, 9.71. $^1$H NMR (CDCl$_3$): $\delta$ 2.32 (s, 6 H, −OCH$_3$), 6.9−7.3 (overlap br s, 8 H, CH phenyl), 8.03 (s, 1H, CH amidine).

**Synthesis of Functionalized Silver *N,N′*-Diphenylformamidinate Complexes.** The silver complexes were synthesized by two different procedures, both based on literature methods. The less hydrophobic complexes were formed in a water/ethanol mixture with potassium

**Table 2.** Ligands, Complexes, and Molecular Weights

| ligand | complex | MW calculated[a] | MW determined[b] |
|---|---|---|---|
| *N,N′*-di(4-methyl)phenylformamidine | **1** | 662.34 | 1024 |
| *N,N′*-di(4-ethyl)phenylformamidine | **2** | 718.44 | 966 |
| *N,N′*-di(4-*n* butyl)phenylformamidine | **3** | | |
| *N,N′*-di(4-*n* hexadecyl)phenylformamidine | **4** | 1503.96 | 2223 |
| *N,N′*-di(4-trifluoromethyl)phenylformamidine | **5** | | |
| *N,N′*-di(3-methoxy)phenylformamidine | **6** | 726.34 | 1292 |
| *N,N′*-di(3-methylmercapto)phenylformamidine | **7** | | |
| *N,N′*-di(2-methoxy)phenylformamidine | **8** | 726.34 | 756 |
| *N,N′*-di(2-methylmercapto)phenylformamidine | **9** | 790.58 | 790 |

[a] Calculated molecular weight based on dimeric structure. [b] Molecular weights determined by vapor pressure osmometry in $CHCl_3$.

hydroxide as the base for deprotonation of the neutral ligand.[30] It appears that this reaction proceeds via an intermediate silver diamidine complex, which is subsequently deprotonated; species corresponding to the proposed intermediate have been structurally characterized by Cotton and co-workers.[31] The complexes having the longer alkyl chains were formed with methanol and/or pyridine as solvent and pyridine as base.[32]

**General Procedure for the Synthesis of Compounds 1, 2, 5−9.** Silver nitrate (25 mmol) was dissolved in 28% ammonium hydroxide (15 mL). A solution of *N,N′*-diphenylamidine (5.6 g, 25 mmol) in ethanol (45 mL) was added slowly. With rapid stirring, a solution of KOH (27.5 mmol) in ethanol/water (40 mL/30 mL) was added over 20 minutes, resulting in a less viscous suspension of white solid. Stirring was continued for a further 10−15 min following addition. The white product was then collected by vacuum filtration, washed with water and/or acetone, and dried in vacuo. Recrystallization was generally carried out from dichloromethane/hexane by cooling a concentrated solution.

**Silver *N,N′*-Di-*p*-tolylformamidinate (1).** Elemental analysis: observed, C, 54.3; H, 4.50; N, 8.18. Calcd for $C_{30}H_{30}N_4Ag_2$: C, 54.4; H, 4.57; N 8.46. $^1$H NMR (CDCl$_3$): $\delta$ 2.15 (s, 12 H, CH$_2$), 6.75 (d, 8 H, CH phenyl), 6.80 (d, 4 H, CH phenyl), 8.01 (t, 2 H, CH amidinate). $^{13}$C NMR: $\delta$ 21.0 (CH$_3$), 121.6 (phenyl), 129.9 (phenyl), 132.2 (phenyl), 148.0 (phenyl), and 162.0 (amidinate C). MS (FAB/3-NBA): *m/z* 555 [AgL$_2$]$^+$, 331 [AgL]$^+$, 225 [L]$^+$.

**Silver *N,N′*-Di(4-ethyl)phenylformamidinate (2).** Elemental analysis: observed, C, 56.0; H, 5.18; N, 7.40. Calcd for $C_{34}H_{38}N_4Ag_2$· 0.5H$_2$O: C, 56.14; H, 5.40; N, 7.70. $^1$H NMR (CDCl$_3$): $\delta$ 1.10 (t, 12 H, CH$_3$), 2.45 (quartet, 8 H, CH$_2$), 6.25 (d, 8 H, CH phenyl), 6.35 (d, 8 H, CH phenyl), 8.04 (t, 2 H, CH amidinate). $^{13}$C NMR: $\delta$ 16.0 (CH$_3$), 28.5 (CH$_2$), 122.0 (phenyl), 128.7 (phenyl), 138.7 (phenyl), 149.0 (phenyl), and 162 (amidinate C). MS (FAB/3-NBA): *m/z* 971 [Ag$_2$L$_3$]$^+$, 825 [Ag$_3$L$_2$]$^+$, 717 [Ag$_2$L$_2$]$^+$, 467 [Ag$_2$L]$^+$, 359 [AgL]$^+$, 251 [L]$^+$.

**Silver *N,N′*-Di(4-*n*-butyl)phenylformamidinate (3).** *N,N′*-Di(4-*n*-butyl)phenylformamidine (6.16 g, 20 mmol) was dissolved in methanol (80 mL) at room temperature. Silver acetate (3.50 g, 21 mmol) was dissolved in pyridine (30 mL) and added dropwise with stirring over 40 min. After 30 min a viscous white suspension was present. When addition of the silver acetate solution was complete, 15 mL of pyridine was added and the mixture was agitated for a further 20 min before filtration. The white product was collected, washed with acetone, and dried in vacuo. Elemental analysis: observed, C, 60.7; H, 6.80; N, 6.40. Calcd for $C_{42}H_{54}N_4Ag_2$: C, 60.7; H, 6.55; N, 6.74. $^1$H NMR (CDCl$_3$): $\delta$ 0.85 (t, 12 H, CH$_3$), 1.28 (m, 8 H, CH$_2$), 1.45 (quintet, 8 H, CH$_2$), 2.40 (t, 4 H, CH$_2$), 6.78 (d, 8 H, CH phenyl), 6.79 (d, 4 H, CH phenyl), 8.02 (t, 2 H, CH amidinate). $^{13}$C NMR: $\delta$ 14.4 (CH$_3$), 22.8 (CH$_2$), 34.1 (CH$_2$), 35.3 (CH$_2$), 122.0 (phenyl), 129.2 (phenyl), 137.3 (phenyl), 148.9 (phenyl), and 162.0 (amidinic C). MS (FAB/3-NBA): *m/z* 832 [Ag$_2$L$_2$]$^+$, 726 [AgL$_2$]$^+$, 415 [AgL]$^+$, 309 [L]$^+$. IR (KBr): 1557 (s), 1570 (s), 1604 (m), 1644 (s) cm$^{-1}$.

**Silver *N,N′*-Di(4-*n*-hexadecyl)phenylformamidinate (4).** *N,N′*-Di-(4-*n*-hexadecyl)phenylformamidine (3 g, 4.7 mmol) was dissolved in pyridine (100 mL) with warming. Silver acetate (0.84 g, 0.5 mmol)

was dissolved in pyridine (30 mL) and the solution was added dropwise with stirring over 40 min to the ligand solution. After 30 min a viscous white suspension was present and, upon complete addition, the mixture was agitated for an additional 10 min before being filtered. The white product was collected, washed with water, followed by acetone, and dried in vacuo. Elemental analysis: observed, C, 71.0; H, 10.8; N, 3.35. Calcd for $C_{90}H_{150}N_4Ag_2$·H$_2$O: C, 71.0; H, 10.1; N 3.68. $^1$H NMR (CDCl$_3$): $\delta$ 0.80 (t, 12 H, CH$_3$), 1.22 (br s, 104 H, CH$_2$), 1.45 (br s, 8 H, CH$_2$), 2.40 (t, 8 H, CH$_2$), 6.77 (d, 8 H, CH phenyl), 6.79 (d, 8 H, CH phenyl), 8.01 (t, 2 H, CH amidinate). MS (FAB/3-NBA): *m/z* 752 [AgL]$^+$, 646 [L]$^+$. IR (KBr): 1559 (s), 1570 (s), 1604 (m), 1646 (s) cm$^{-1}$.

**Silver *N,N′*-Di(4-trifluoromethyl)phenylformamidinate (5).** Elemental analysis: observed, C, 40.4; H, 1.80; N, 6.00. Calcd for $C_{30}H_{18}N_4Ag_2F_{12}$·0.5H$_2$O: C, 40.6; H, 2.16; N, 6.31. $^1$H NMR (pyridine-$d_5$): $\delta$ 7.6 (d, 8 H, CH phenyl), 7.7 (d, 8 H, CH phenyl), 9.0 (s, 2 H, CH amidinate). MS (FAB/3-NBA): *m/z* 878 [Ag$_2$L$_2$]$^+$, 547 [Ag$_2$L]$^+$, 439 [AgL]$^+$, 334 [L]$^+$.

**Silver *N,N′*-Di(3-methoxy)phenylformamidinate (6).** Elemental analysis: observed, C, 48.8; H, 4.28; N, 7.30. Calcd for $C_{30}H_{30}N_4O_4$-Ag$_2$·H$_2$O: C, 48.4; H, 4.33; N, 7.53. $^1$H NMR (CDCl$_3$): $\delta$ 3.56 (s, 12 H, −OCH$_3$), 6.3−6.5 (overlap, 12 H, CH phenyl), 6.92 (dd, 4 H, CH phenyl), 8.15 (t, 2 H, CH amidinate). MS (FAB/3-NBA): *m/z* 365 [AgL]$^+$.

**Silver *N,N′*-Di(3-methylmercapto)phenylformamidinate (7).** Elemental analysis: observed, C, 44.4; H, 3.88; N, 7.00. Calcd for $C_{30}H_{30}N_4S_4Ag_2$·H$_2$O: C, 44.6; H, 3.99; N, 6.93.

**Silver *N,N′*-Di(2-methoxy)phenylformamidinate (8).** Elemental analysis: observed, C, 49.7; H, 4.08; N, 7.60. Calcd for $C_{30}H_{30}N_4O_4$-Ag$_2$: C, 49.6; H, 4.16; N, 7.71. $^1$H NMR (CDCl$_3$): $\delta$ 3.66 (s, 12 H, −OCH$_3$), 6.8 (overlap br s, 8 H, CH phenyl), 6.9 (d, 4 H, CH phenyl), 7.21 (d, 4 H, CH phenyl), 8.27 (br s, 2 H, CH amidinate). MS (FAB/3-NBA): *m/z* 726 [Ag$_2$L$_2$]$^+$, 621 [AgL$_2$]$^+$, 471 [Ag$_2$L]$^+$, 363 [AgL]$^+$, 257 [L]$^+$.

**Silver *N,N′*-Di(2-methylmercapto)phenylformamidinate (9).** Elemental analysis: observed, C, 45.9; H, 3.53; N, 7.59. Calcd for $C_{30}H_{30}N_4S_4Ag_2$: C, 45.6; H, 3.82; N, 7.09. $^1$H NMR (CDCl$_3$): $\delta$ 2.22 (s, 12 H, −SCH$_3$), 6.88−7.10 (overlap br s, 12 H, CH phenyl), 7.21 (d, 4 H, CH phenyl), 8.23 (br s, 2 H, CH amidinate). MS (FAB/3-NBA): no assignable peaks.

## Results and Discussion

The silver(I) complexes (**1**−**9**), shown in Table 2 and Figure 3, were prepared by literature procedures with solvent and concentration variations to accommodate differences in solubility due to the increase in hydrophobicity of long-chain alkyl derivatives. All complexes are white powders and show varying degrees of light sensitivity, consistent with a corresponding variation in thermal stability. FAB mass spectra were generally consistent with dimeric structures. The predominant ion was often produced by fragmentation to give a combination of ligands and silver ions of lower mass than an Ag$_2$L$_2$ dimer, most commonly [AgL$_2$]$^+$. In the case of silver *N,N′*-di(4-ethyl)-phenylformamidinate, peaks corresponding to [Ag$_2$L$_3$]$^+$ and

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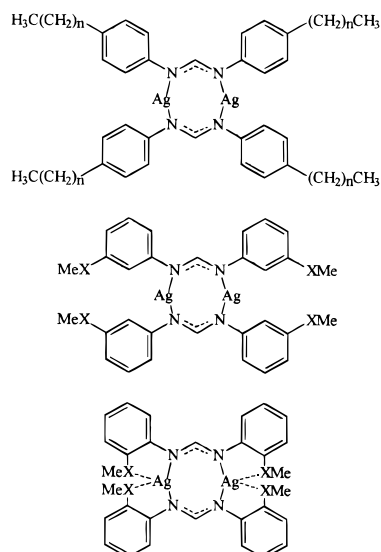(32) Bradley, W.; Wright, I. *J. Chem. Soc.* **1956**, 640.

**Figure 3.** Amidinate dimer structural types (X = O or S).

[Ag$_3$L$_2$]$^+$ were found. These could be fragments of larger species in solution or aggregates formed during the mass spectrometry experiment.

**Crystallographic Studies.** Our determination of the crystal structure of **8** duplicates that reported in a recent publication focused on the photophysical properties of the compound.[33] Compound 8 has an approximate noncrystallographic 2-fold axis of symmetry along the Ag–Ag axis (Figure 4). Each silver atom is four-coordinate, bound to two amidinate nitrogens and two methoxy oxygens. The interactions with N are considerably stronger than those with O, with Ag–N of 2.11 Å (mean) and Ag–O in the range 2.691–2.894 Å; these Ag–O bond lengths are greater than the intermolecular Ag–O distances found in the silver carboxylate step polymers, e.g., 2.60 Å in silver stearate[3i] and 2.417 Å in silver phenoxyacetate. Similar long Ag–O bond lengths to ether O-donors have been observed in mixed-donor crown ether ligands.[34] The Ag–Ag distance is increased relative to that in previously characterized amidinate dimers (2.780 Å, compared to 2.65–2.70 Å).[12,14] It is slightly shorter than the closest contacts observed in metallic silver (2.88 Å).[35]

The eight-membered Ag$_2$(NCN)$_2$ ring in this structure is slightly twisted about the C–C axis, in contrast to the virtually planar arrangement in the *N,N′*-di-*p*-tolylformamidinate dimer.[14] In that structure also, the phenyl rings are only slightly twisted from the Ag$_2$(NCN)$_2$ plane, whereas in **8** the phenyl rings are twisted to angles of 35.7°–46.9° to this plane, placing a methoxy group on either side of the plane. This twist is clearly necessary to place the 2-methoxy substituents at suitable distances from the Ag atoms.

Compound **9** similarly crystallizes with a noncrystallographic 2-fold axis along the Ag–Ag axis (Figure 5). The silver atoms are again four-coordinate, bound to a nitrogen donor from each amidinate ligand and a thioether donor, also with relatively long Ag–S bonds (2.79–2.99 Å). However, such Ag–S bond lengths are similar to those observed for thioether and thiocrown complexes.[34,36] As with **8**, the phenyl groups are twisted out of the Ag$_2$(NCN)$_2$ plane, with rather variable dihedral angles

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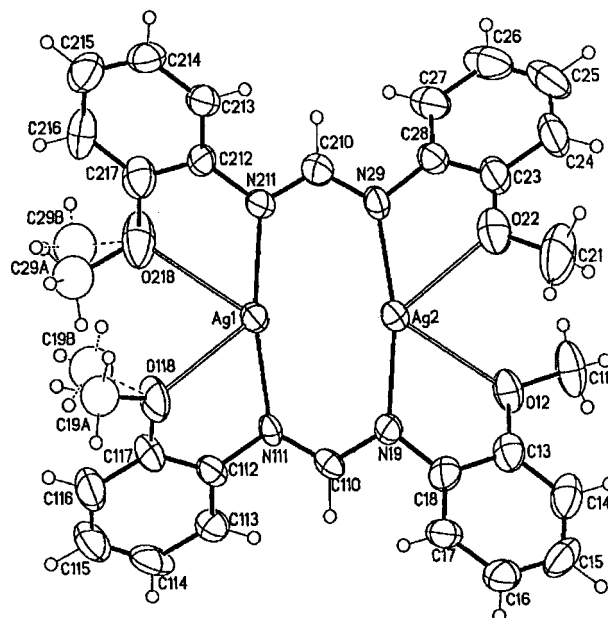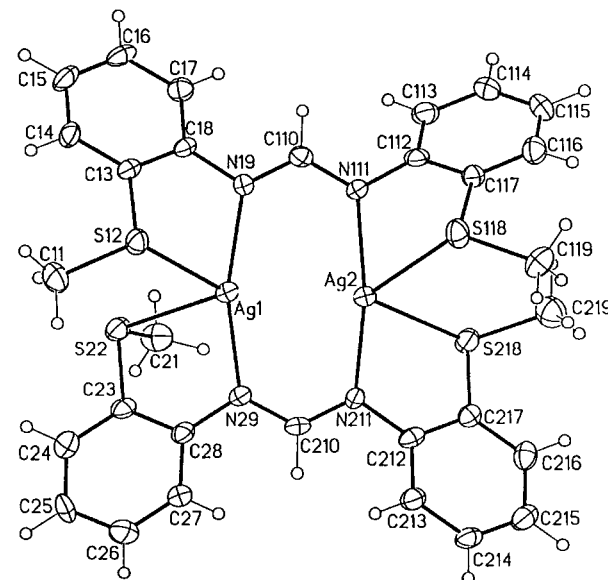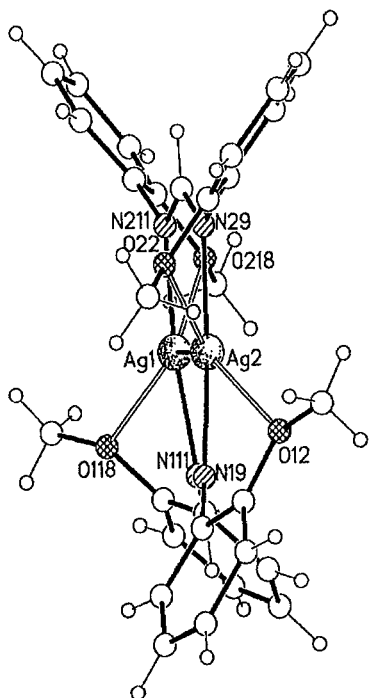


**Figure 4.** View of **8** showing atomic numbering. Thermal ellipsoids are drawn at the 50% level. Selected bond lengths (in angstroms): Ag-(1)−N(211), 2.104(5); Ag(1)−N(111), 2.123(5); Ag(1)−O(118), 2.691-(5); Ag(1)−Ag(2), 2.7801(7); Ag(1)−O(218), 2.894(6); Ag(2)−N(19), 2.118(5); Ag(2)−N(29), 2.127(5); Ag(2)−O(22), 2.700(5); Ag(2)−O(12), 2.742(5). Selected angles (in degrees): N(211)−Ag(1)−N(111), 167.2(2); N(111)−Ag(1)−O(118), 65.1(2); N(211)−Ag(1)−Ag(2), 85.90(14); N(111)−Ag(1)−Ag(2), 81.99(13); N(211)−Ag(1)−O(218), 63.3(2); O(118)−Ag(1)−O(218), 81.8(2); N(19)−Ag(2)−N(29), 166.8-(2); N(29)−Ag(2)−O(22), 65.4(2); N(19)−Ag(2)−O(12), 65.2(2); O(22)−Ag(2)−O(12), 79.2(2); N(19)−Ag(2)−Ag(1), 85.32(13), N(29)−Ag(2)−Ag(1), 81.5(2).



**Figure 5.** View of **9** showing atomic numbering. Thermal ellipsoids are drawn at the 50% level. Selected bond lengths (in angstroms): Ag-(2)−N(211), 2.147(4); Ag(2)−N(111), 2.148(4); Ag(2)−S(118), 2.988-(2); Ag(1)−Ag(2), 2.8050(4); Ag(2)−S(218), 2.862(2); Ag(1)−N(19), 2.194(4); Ag(1)−N(29), 2.191(4); Ag(1)−S(22), 2.7896(14); Ag(1)−S(12), 2.8187(14). Selected angles (in degrees): N(211)−Ag(2)−N(111), 169.15(14); N(211)−Ag(2)−S(218), 70.47(11); N(19)−Ag(1)−N(29), 164.15(14); N(19)−Ag(1)−S(22), 117.19(10); N(111)−Ag(2)−S(218), 113.91(11); N(29)−Ag(1)−S(12), 121.46(11); N(29)−Ag(1)−S(22), 75.57(10); N(19)−Ag(1)−S(12), 70.79(10); S(22)−Ag(1)−S(12), 86.72(5).

(33.6°−57.4°); each silver(I) center has distorted tetrahedral geometry. The Ag–Ag distance is 2.805 Å and N−Ag−N

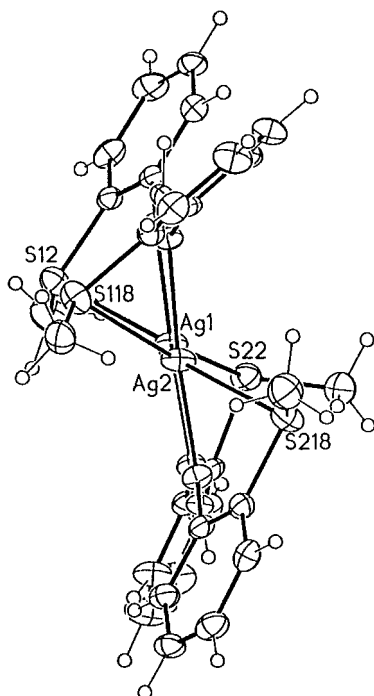**Figure 6.** View of **8** showing the orientation of the phenyl rings.



**Figure 7.** View of **9** showing the orientation of the phenyl rings, contrasted to Figure 6.

angles are similar to those in the oxo complex, 164.15° and 169.15°. Surprisingly, **8** and **9** differ in the conformation of the amidinate ligands. Whereas in **8**, the phenyl rings on one amidinate ligand are twisted in opposite directions, in **9** the thioether groups lie on the same side of the $Ag_2(NCN)_2$ plane, as shown in Figures 6 and 7. This demonstrates that these ligands may coordinate in more than one conformation, although the silver coordination geometry is little changed. It should be noted that the $^1$H NMR spectra suggest that these conformations may exchange in solution.

Despite Cotton's conclusion[14] that complexes of this type contain no Ag–Ag interactions, one explanation for the increase

in Ag–Ag distance when external bonds to O or S are formed is that these ligand atoms are donating electron density into an antibonding Ag–Ag orbital, weakening a metallic bond between the two silver atoms. Alternatively, it may be that the steric constraints on the positions of the O or S atoms prevent them from reaching an ideal distance from the Ag atoms; the attractive O/S to Ag interaction then pulls the Ag atoms slightly apart. Neither **8** nor **9** shows intermolecular interactions involving the silver atoms.

**$^1$H NMR Studies Including Variable Temperature.** $^1$H NMR spectra of all *N,N′*-di(4-*n*-alkyl)phenylformamidinate silver complexes (**1**–**4**) synthesized showed a splitting of the −N−(CH)−N− signal into a triplet. Coupling to pairs of $^{107}$-Ag ($I = \frac{1}{2}$, 51.8%) and $^{109}$Ag ($I = \frac{1}{2}$, 48.2%) centers is postulated to account for this splitting. Confirmation was obtained by comparison of spectra at 300 and 400 MHz ($J = 16$ Hz) and by the collapse of the signal on broadband irradiation. Attempts to collect an HMQC $^{109}$Ag spectrum for complex **2** have been unsuccessful. The presence of the proposed coupling is normally indicative of high kinetic stability of the dimeric compounds in solution. Previously, kinetically stable complexes in which the silver(I) is in the appropriate orientation with respect to a proton have shown $^1$H−$^{107/109}$Ag coupling, thus allowing the collection of polarization transfer spectra.[37−41] Since direct observation of $^{109}$Ag NMR spectra is inhibited by the long relaxation times ($t = 1000$ s), the use of relaxation agents can be helpful,[42,43] but the possibility of binding to the silver(I) center has limited such applications in the past.

The coupling of silver atoms to the proton in a bridging formamidinate ligand has been observed by Vrieze et al. in a silver–platinum compound with an Ag–Pt bond in which the formamidinate ligand bridged the two metal centers.[40] Coupling was observed to the silver center [−N−(CH)−N− doublet, $J = 8$ Hz] and an INEPT $^{109}$Ag spectrum was obtained. Although both $^{107}$Ag and $^{109}$Ag caused splitting, the signals coincided as a result of the low ratio of their gyromagnetic constants and the small $J$ value and only a doublet was observed. This is consistent with our complexes where a triplet is observed; however, the triplet shows broadening not seen in the previous case, possibly due to an extremely broad unresolved $^{109}$Ag signal.

Silver(I) *N*-alkyl-*N′*-phenylformamidinate complexes demonstrate high lability in solution and their equilibria were studied in unsymmetric complexes by Vrieze and co-workers.[30] Variable-temperature $^1$H and $^{13}$C NMR spectra showed that several species exist in equilibrium, and these were postulated to include dimeric and tetrameric forms. It was observed that the −N−(CH)−N− peak in the proton spectrum is split, displaying as many as seven separate peaks on cooling. In this

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**Table 3.** DSC and TGA Data Summary

| complex | phenyl substituent | DSC (°C) | TGA onset (°C) | % lost/% residue | theoretical % residue[a] |
|---|---|---|---|---|---|
| 1 | 4-methyl | 187.2 exo | 155 | 6.1 | |
| | | | 200 | 48.4 | |
| | | | residue | 44.1 | 32.61 |
| 2 | 4-ethyl | 185.1 exo onset | 210 | 58.0 | |
| | | | residue | 37.4 | 30.02 |
| 3 | 4-*n*-butyl | 166.4 endo | 200 | 66.2 | |
| | | | residue | 27.4 | 26.00 |
| 4 | 4-*n*-hexadecyl | 88.1 endo, reversible | 270 | 53.9 | |
| | | | residue | 16.1 | 14.34 |
| 5 | 4-trifluoromethyl | 254.5 endo | 250 | 66.2 | |
| | | | residue | 27.5 | 24.65 |
| 6 | 3-methoxy | 182.9 endo[b] | 100 | 2.9 | |
| | | | 200 | 55 | |
| | | | residue | 42.1[c] | 29.74 |
| 7 | 3-methylmercapto | 234.8 endo[a] | 250 | 48.6 | |
| | | | residue | 44 | 27.39 |
| 8 | 2-methoxy | 116 endo | 120 | 5.2 | |
| | | 194.1 endo[b] | 190 | 45.6 | |
| | | | residue | 32.9[b] | 24.65 |
| 9 | 2-methylmercapto | 247.9 endo[b] | 270 | 67.5 | |
| | | | residue | 32.4 | 27.39 |

*[a]* Based on decomposition to Ag metal. *[b]* The endotherm leads directly into an exotherm. *[c]* The residual mass continues to decrease above 600 °C.

case coupling to the Ag centers was not considered, and the increased lability with ligands containing an *N*-alkyl substituent probably prevents such coupling from appearing. In the variable-temperature ¹H spectra of **2** (recorded between 223 and 303 K), no additional splitting, sharpening, or broadening of the peak was observed. Thus we tentatively conclude that the eight-membered ring structure that unites pairs of silver ions with pairs of ligands is kinetically inert under these conditions.

We would expect that incorporating additional donors into the ligand structure would increase the stabilities of the silver complexes (Table 2, Figure 3) and inhibit any tendency of the ligands to undergo exchange in solution. The room-temperature ¹H NMR spectrum of **9** (which has −SMe groups ortho to the amidinate nitrogens) shows a singlet for the amidinate proton [−N−C(H)−N-] suggesting no coupling to the silver centers. However, variable-temperature proton spectra of **9** (recorded at 10 K intervals between 227 and 308 K) reveals coupling to the pair of silver ions. On cooling, the singlet [−N−C(H)-N-] resonance at 8.2 ppm first broadens and then sharpens to form a triplet ($J$ = 14.8 Hz) at ca. 240 K. The corresponding −OMe derivative, **8**, shows a similar behavior with the appearance at low temperature of a triplet at 8.2 ppm ($J$ = 15.5 Hz) due to coupling to the silver centers. However, the triplet was resolved at a substantially higher temperature, ca. 270 K, and an additional triplet of lower intensity appears at 7.98 ppm, along with accompanying phenyl resonances upfield relative to the stronger phenyl signals. The ratio of the integrated peak areas for the two triplet signals is ca. 4:1 at 227 K.

An explanation of the variable temperature behavior exhibited by **8** and **9** must take into account the inherent lability of silver-(I). However, the high stability of the eight-membered ring unit is also well demonstrated in related systems (above). The appearance of coupling at a higher temperature for **8** suggests a less favorable exchange process than that occurring for **9**. It can be suggested that the exchange involves the silver atom moving toward the ether or thioether donor while simultaneously undergoing Ag−N bond cleavage, a structure change that would result in loss of coupling. Since Ag⁺ binds preferentially to sulfur over oxygen, the thioether groups of **9** would be expected to compete with the nitrogen donors more effectively than would

the oxoethers of **8**. Therefore **9** would continue to exchange at lower temperatures than **8**.

The minor triplet appearing at 7.98 ppm in the spectra of **8** can be explained by the existence of a conformational isomer. The crystal structures of **8** and **9** demonstrate different conformations (Figures 6 and 7). An equilibrium between these two conformations is suggested, with the more stable form, corresponding to the crystal structure of **8**, giving the downfield resonance at 8.2 ppm; the same value is observed in the thioether derivative. However, because the chemical shift for the CH amidinate proton for the upfield resonance is similar to that observed for compounds having no additional donors (**1**−**4**, 8.0 ppm), the preferred explanation for the minor component involves a structure with the methoxy oxygens dissociated, leaving 2-coordinate silver centers.

The proton spectrum of *N,N′*-di(3-methoxy)phenylformamidinate silver(I), **6**, shows splitting of the amidinate proton (8.1 ppm) by coupling to silver at room temperature as observed for complexes of the 4-alkyl-substituted ligands. Solution studies of the *N,N′*-di(3-methylmercapto)phenylformamidinate silver-(I) complex were not possible due to its insolubility even in N-donor solvents such as pyridine. Such insolubility suggests a similarity to silver carboxylates that form polymeric arrays in the solid state. It is also consistent with the preference of silver(I) for binding to thioether over oxoether donor atoms.

**Molecular Mass in Solution.** Molecular masses in solution were determined by vapor pressure osmometry for **1**, **2**, **4**, **6**, **8**, and **9**. The values are given in Table 2 along with the calculated molecular mass for the dimeric species. Compounds **1**, **2**, **4**, and **6** show modest aggregation to higher mass species in solution. The molecular mass of the 4-alkylphenyl-substituted complexes **1**, **2**, and **4** are approximately 1.5 times the mass of the dimeric species. It is reasonable to suggest that a mixture of dimers and tetramers is present since these are the two predominant structural types in the solid state for the triazenate and amidinate complexes of Cu(I), Ag(I), and Au(I). However, the tetrameric complexes do not contain the eight-membered rings of the dimers, so the higher molecular mass could be attributed to a simpler aggregation of dimeric species in solution in which their eight-membered rings are retained. In such an aggregation, a two-coordinate silver ion would form an

additional intermolecular interaction to an amidinate nitrogen in another dimer. Complex **6** could also aggregate in solution via intermolecular interactions between silver ions and methoxy groups; this possibly accounts for the higher mass observed relative to **1**, **2**, and **4** (1.8 times the mass of the dimer as opposed to roughly 1.5). In solution, **8** and **9** show masses closely corresponding to the dimeric species. This shows the stabilization of the unique dimeric species by the additional coordinated groups. The steric constraints imposed by the coordinated groups in the 2-position would also inhibit formation of higher oligomers.

**Thermal Studies.** Silver carboxylates have been shown to decompose at 200–350 °C to silver(0), carbon dioxide, and radicals (e.g., silver trifluoroacetate decomposes at 260 °C to give silver(0), carbon dioxide, and trifluoromethyl radicals).[44] Differential scanning calorimetry and thermal gravimetric analysis were used to examine the new silver amidinate complexes. The only previous data on thermal decomposition of amidinate complexes, to our knowledge, is provided by Kilner et al,[45] examining copper(I) and copper(II) complexes of benz-, acet-, and formamidinate ligands. When mass loss could be assigned, decomposition involved either the loss of complete amidinate ligands or partial decomposition of ligands still coordinated to the metal center.

The decomposition onset as demonstrated by DSC and TGA was taken to indicate the thermal stability of a compound (Table 3) and used as a measure of the relative stability of the two- and four-coordinate silver amidinate complexes. For the alkyl chain substituents, increasing *n* from 1 to 4 led to an increasing onset temperature for decomposition, starting around 150 °C. Stability apparently increases on further lengthening of the chain. For *n* = 16, in addition to the substantial increase in decomposition onset temperature, the DSC shows an endotherm at 88.1 °C. This was initially attributed to a melting point due to the presence of the long alkyl chain ligands. The apparent melting point was investigated by heating the sample to 95 °C, immediately cooling to room temperature, and reheating, which reproduced the endotherm peak. The integrated peak intensity, however, decreased by a factor of 2, implying some decomposition, and a new peak (exotherm) had now appeared at 72 °C. No corresponding weight loss was observed at this temperature in the TGA. An attempt to determine the melting point with a standard melting point apparatus was unsuccessful because decomposition, possibly light-induced, occurred around the melting temperature.

In contrast to these 4-alkylphenyl chain derivatives, it appears that additional stability results from the addition of an electron-withdrawing group at the 4-position. The 4-(trifluoromethyl)-phenyl complex, **5**, does not exhibit decomposition until a higher temperature is reached; the first endotherm and weight loss appear at 254 °C. The compounds containing methylmercapto groups, **7** and **9**, show the greatest stability increase relative to **1**–**4**. The insoluble complex **7**, where polymeric cross-links via the 3-methylmercapto substituent are suggested, shows a marginally lower thermal stability than **9**. The methoxy com-

pounds **6** and **8** show a similar pattern with endotherms appearing at 183 and 194 °C, respectively.

TGA showed a complicated one-stage decomposition for all the complexes except **8**, which has a two-stage decomposition. Small initial losses (3–6%) were observed for **1**, **6**, and **8**, which are attributed to residual solvent removal (consistent with the analysis of bulk samples), Kilner et al.[45] found that the copper-(I) complexes gave thermograms that indicated a two-stage decomposition process for acetamidinate complexes, one stage for benzamidinate complexes and intermediate for formamidinate complexes.

For compounds **1**–**4** the weight loss corresponds to eventual removal of both amidinate ligands, although no sequential or fragment loss could be identified. In several cases small weight loss continues past the main decomposition, as can be seen by the high residual percentage compared to theoretical conversion to silver metal. Kilner et al.[45] observed that the percentage weight loss could not always be assigned to an amidine fragment and the residue was often found to contain a small percentage of carbon, hydrogen, and/or nitrogen; however, in the case of the copper(I) *N′,N*-diphenylbenzamidinate complex the loss of mass gave a residue corresponding to copper metal. This is similar to our results, which do not allow straightforward assignments.

## Conclusions

In the nine silver complexes of phenyl-functionalized *N,N′*-diphenylformamidinate, the thermal stability of the complexes increases with lengthening of the 4-alkyl-substituted chain and with the addition of an electron-withdrawing substituent in the 4-position or a coordinating group in the 2- or 3-position. The methylmercapto substituent shows more favorable bonding interactions and a consequent increase in stability. This is also evident from the insolubility of the 3-methylmercapto complex and the structural data for **9**. With the 3-methylmercapto complex the potential for formation of a polymeric network exists, which could involve dimeric units connected by sulfur donor atoms. Complexes **8** and **9** shows the predicted solid-state dimeric structure with four-coordinate silver centers.

Molecular mass measurements demonstrate the presence of larger aggregates in solution for compounds **1**–**4** and **6**. NMR studies imply kinetic stability for compounds **1**–**4** and **6**, suggesting retention of the eight-membered ring dimeric unit. Their aggregation in solution is attributed to intermolecular interactions (Ag–N bonding) between dimeric units. The complexes with additional coordinating substituents, **8** and **9**, give the expected mass for discrete dimeric species in solution, indicating that the additional ligating atoms thwart any tendencies toward further interactions and aggregation.

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(45) Kilner, M.; Pietrzykowski, A. *Polyhedron* **1983**, *2*, 1379. Halfpenny, J. *Acta Crystallogr.* **1995**, *C51*, 2542.