139199-88-5; **16**, 139242-65-2; **17**, 139199-89-6; **18**, 139199-90-9; **19**, 139199-91-0; **20**, 139199-92-1; **21**, 139199-93-2; **22**, 139242-66-3; **23**, 139242-67-4; **24**, 139242-68-5; ^{199}Hg, 14191-87-8; Hg, 7439-97-6; Ru, 7440-18-8.

Supplementary Material Available: Tables of analytical (Table S-I), ^{1}H NMR (Table S-II), and IR data (Table S-III), complete positional parameters, bond distances, bond angles, thermal parameters for the non-hydrogen atoms, hydrogen atom positions with their isotropic thermal parameters, and complete crystal data for both structures (17 pages); tables of structure factors (52 pages). Ordering information is given on any current masthead page.

Contribution from the Anorganisch Chemisch Laboratorium, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, Debye Research Institute,
Department of Metal-Mediated Synthesis, and Bijvoet Research Institute,
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Stereoregular Coordination Polymers Formed on Binding of Peptide-Based Polydentate Ligands to Silver(I) and Copper(I). X-ray Structure of ([Ag{*N*-[*N*-((5-methyl-2-thienyl)methylidene)-L-methionyl]histamine}]$^+$[O_3SCF_3]$^-$·MeOH)$_\infty$ and a Solution Structure Study[1]

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Received October 11, 1991

From the 1:1 metal salt to ligand reactions of $Ag^IO_3SCF_3$ or $Cu^IO_3SCF_3$ with the polydentate donor ligand system *N*-[*N*-((5-R-thienyl)methylidene)-L-methionyl]histamine (=(5R)Th-Met-Histam; R = H, Me, Me_3Si) stable coordination complexes have been obtained. The solid-state structure of [Ag{(5Me)Th-Met-Histam}](OTf) was determined. ([$C_{16}H_{22}N_4S_2Ag$]$^+$[O_3SCF_3]$^-$·CH_4O)$_\infty$ crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 11.339$ (1) Å, $b = 13.122$ (1) Å, and $c = 17.451$ (1) Å. The complex cation has a polymeric structure that results from each ligand molecule stretching out over three different Ag(I) cations. Each Ag(I) center is sp^2 hybridized and trigonally coordinated by an imidazole N [2.218 (4) Å], an imine N [2.378 (5) Å], and a methionine S atom [2.509 (2) Å]. There is an additional weak interaction with an amide O atom [2.568 (4) Å], which is situated above the trigonal plane. A more distant thiophene S atom lies on the other side of the plane [3.081 (2) Å]. Viewed from S to O along an axis perpendicular to the trigonal plane the configuration of all Ag(I) centers is *R*; this defines a Δ-helix structure for the polymeric cation. By use of a combination of spectroscopic techniques (^{19}F, ^{109}Ag, and ^{1}H NMR, UV, CD, and optical rotation) and other measurements (vapor pressure osmometry and conductivity), it is established that the complexes [Ag{(5R)Th-Met-Histam}](OTf) (R = H, Me, Me_3Si) in solution have an oligomeric structure that is similar to the polymeric structure of [Ag{(5Me)Th-Met-Histam}](OTf) in the solid state. The average chain length of the oligomer is a function of complex concentration and temperature; for the (5Me)Th-Met-Histam complex at 318 K the chain length varies from 1 unit in dilute solution to at least 11 units at a concentration of 0.14 mol·L^{-1}. Comparison of the X-ray structure conformations of (5Me)Th-Met-Histam as a free molecule and as ligand in this Ag(I) complex shows that, apart from one rotation, the changes are minimal. The self-assembly process, which affords the polycationic Ag(I) coordination complexes through a simultaneous, configurationally unique arrangement of different ligating sites from three separate sources around each cationic nucleus, manifests a degree of self-organization that has so far not often been encountered in synthetic coordination chemistry. The Cu(I) complexes have structures that are comparable to those of their Ag(I) counterparts, although the average chain length under identical conditions may be less. An intramolecular electron shift equilibrium mechanism, involving Cu(I)-imidazole and Cu(II)-imidazole$^{\bullet-}$ transitions, is proposed to explain the line broadening present in the ^{1}H NMR spectra of the Cu(I) complexes.

Introduction

The field of supramolecular chemistry, as defined among others by Lehn,[2] is a rapidly growing area. An aspect of the "chemistry beyond the molecules", involves the concept of molecular self-assembly, i.e., the formation of specifically organized aggregates from small basic building blocks. Self-assembly is an important feature in living nature,[3] e.g., the double helix formation of nucleic acids, yet the number of examples in synthetic chemistry is still limited. Recently Lehn and co-workers have reported on "helicates", coordination complexes of the group 11 cations Ag(I) or Cu(I) with oligobipyridines, whose structures turn out to be inorganic double helices.[3,4]

We had already reported extensively on a similar double-helix effect that occurs in binuclear Ag(I) and Cu(I) coordination complexes of the neutral N_4 donor ligand (pyridine-2-CH=N)$_2$(*R*),(*S*)-1,2-cyclohexane.[5] In these dicationic complexes with an [$M_2\{N_4\}_2$]$^{2+}$ stoichiometry the ligand acts as a bis(N_2-bidentate) donor. In the free ligand the conformation of the chiral cyclohexanediyl bridging group enforces a more or less perpendicular arrangement of both chelating functions, and upon complexation of this ligand a helical structure results with both metal centers having either the Δ or the Λ configuration.[6]

The related N_2S_2 donor ligand,[7] in which thiophene replaces pyridine, gives rise to a dicationic [$M_2\{N_2S_2\}_2$]$^{2+}$ complex similar

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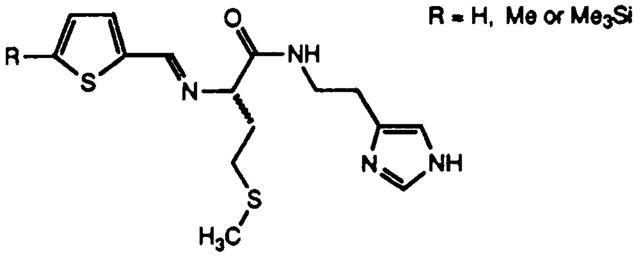

Figure 1. (5R)Th-Met-Histam.

to its N_4 counterpart. Furthermore, in contrast to the latter ligand, it is also possible to isolate a monocationic complex with $[M\{N_2S_2\}_2]^+$ stoichiometry, in which the metal center is predominantly coordinated by two imine nitrogen atoms. In an elaborate study of related copper and silver complexes with N,S donor ligands containing a single thienylmethylidene–amino moiety,[8] we have shown that stabilization of the dicationic complex with N_2S_2 ligands is entirely due to the specific ligand conformation induced by the cyclohexanediyl unit; unlike the imine N atoms, the affinity of the thiophene S atoms for coordination to group 11 monocations is negligible.

The apparent strong influence of certain conformational restrictions in a ligand system on the structure of its coordination complexes prompted us to investigate the coordination behavior of less symmetric, polydentate N_2S_2 analogues. Suitable candidates were to contain a thienylmethylidene–amino unit (as in the N,S and N_2S_2 ligands, vide supra), as well as other potential N and S donor functions, and a stereogenic center whose configuration could be easily controlled. On the basis of these criteria, we designed and synthesized *N*-[*N*-((5-R-2-thienyl)methylidene)-L-methionyl]histamine (R = H, Me or Me_3Si),[9] see Figure 1, abbreviated in this publication as (5R)Th-Met-Histam.

In (5R)Th-Met-Histam three arms, connected to one stereogenic carbon center, in casu methionine C_α, each provide a different ligating group: the "histamine–amide" fragment and the methionine side chain contain an imidazole-*N* and a thioether-*S* donor atom, respectively, and the thienylmethylidene–amino moiety is a potentially bidentate N,S donor. CPK molecular model studies indicated that this ligand could fold to provide a cavity in which an N,N′,S,S′ donor array would be available for coordination to a single metal atom. However, an X-ray structure determination of the uncomplexed (5Me)Th-Met-Histam molecule shows a conformation in the solid state[9] that suggests that as a ligand it would be more likely to coordinate to several metal centers at the same time.

This paper reports a study of the coordination properties of molecules of the (5R)Th-Met-Histam type with the salts $Ag^IO_3SCF_3$ and $Cu^IO_3SCF_3$.[10] The resulting coordination complexes turn out to be good examples of self-assembled superstructures. Experimental data concerning the structural features and polymeric nature of these complexes in the solid state (X-ray, IR, MS) and in solution (^1H, ^{19}F, and ^{109}Ag NMR, UV, CD, optical rotation, vapor pressure osmometry, and conductivity measurements) are presented and discussed in relation to the structure of the free ligand.

Experimental Section

Preparation of the Compounds. Unless denoted otherwise, solvents used were freshly distilled and stored under nitrogen atmosphere. The ligands of the type *N*-[*N*-((5-R-2-thienyl)methylidene)-L-methionyl]histamine (=(5R)Th-Met-Histam; R = H, Me, Me_3Si) were synthesized according to a method reported separately.[9] 5-Trimethylsilyl-2-thiophenecarbaldehyde[11] and copper(I) trifluoromethanesulfonate–0.5-benzene[12] were synthesized by literature procedures. Commercially available silver(I) trifluoromethanesulfonate was used without purification. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

[Ag{*N*-[*N*-((5-R-2-thienyl)methylidene)-L-methionyl]histamine}](O_3SCF_3). The synthesis of [Ag{(5Me)Th-Met-Histam}](OTf) has been published in a preliminary communication.[1b] However, the procedure has since been simplified, and this revised version is given here. At room temperature, solutions of (5Me)Th-Met-Histam (0.99 g, 2.83 mmol) in MeOH (p.a. grade, 10 mL) and of AgO_3SCF_3 (0.73 g, 2.83 mmol) in MeOH (p.a. grade, 10 mL) were mixed, with exclusion of direct light. After the mixture was stirred for 0.5 h, diethyl ether and hexane (approximately 10 and 2 mL, respectively) were added. Subsequent cooling to 4 °C for 15 h allowed isolation of faintly colored crystals of $([Ag\{(5Me)Th\text{-}Met\text{-}Histam\}]^+[OTf]^-\cdot MeOH)_\infty$. When dried in vacuo, the crystals turn into an amorphous white powder due to loss of MeOH from the crystal lattice.

Anal. Found (calcd for $C_{17}H_{22}AgF_3N_4O_4S_3$): C, 32.58 (33.61); H, 3.66 (3.65); N, 8.94 (9.22); F, 9.17 (9.38); S, 15.39 (15.83).

[Ag{(5H)Th-Met-Histam}](OTf) and [Ag{($5Me_3Si$)Th-Met-Histam}](OTf) were obtained similarly. ^1H and ^{19}F NMR data for the Ag(I) complexes are given in Table IV.

[Cu{*N*-[*N*-((5-R-2-thienyl)methylidene)-L-methionyl]histamine}](O_3SCF_3). The synthesis of [Cu{(5H)Th-Met-Histam}](OTf) is described here in detail. Under an atmosphere of dry nitrogen, a solution of $CuO_3SCF_3\cdot{}^1/_2C_6H_6$ (0.43 g, 1.71 mmol) in benzene (15 mL) was added to a stirred suspension of (5R)Th-Met-Histam (0.57 g, 1.70 mmol) in benzene (10 mL) at room temperature. Immediately yellow solids as well as some orange glasslike substance separated from the benzene. The reaction mixture was stirred for 30 min at room temperature, after which the benzene layer was separated by decantation, and the remaining material was dried in vacuo, for several hours. During this stage the glassy solid turned into powder. Anal. Found (calcd for $C_{16}H_{20}CuF_3N_4O_4S_3$): C, 33.44 (35.00); H, 3.76 (3.67); F, 10.78 (10.38); N, 9.06 (10.20); S, 16.27 (17.52). Cu{(5Me)Th-Met-Histam}](OTf) and [Cu{($5Me_3Si$)Th-Met-Histam}](OTf) were synthesized following the same procedure.

All copper(I) complexes proved to be rather unstable in methanolic solutions when allowed to stand for prolonged periods (hours). NMR experiments could be carried out, but attempts to recrystallize these complexes from the same solvent mixture that was used for their silver(I) counterparts failed in all cases but one. Only once, the Me_3Si-substituted compound (seemingly the most stable one) afforded tiny orange crystals, but these were unfortunately of too poor a quality to allow an X-ray structure determination. ^1H and ^{19}F NMR data for the Cu(I) complexes are given in Table IV.

Physical Measurements. All NMR experiments were carried out on CD_3OD solutions at 298 K unless denoted otherwise. ^1H NMR spectra were recorded on Bruker AC100 and WM250 spectrometers with tetramethylsilane as external reference. ^{19}F NMR spectra were recorded on a Bruker AC100 spectrometer, $CFCl_3$ being used as external reference. When Cu(I) complexes were being measured, small strips of copper wire were introduced into the NMR tubes to prevent or slow down oxidation; the presence of copper metal did not have a noticeable effect on the sample homogeneity. ^{109}Ag NMR of [Ag{(5Me)Th-Met-Histam}](OTf) was recorded on a Bruker AC100 spectrometer by direct measurement of natural abundance ^{109}Ag: 4.66 MHz, 10-mm tube, 0.61 g of the complex in 2.7 g of CD_3OD ($c = 0.3$ mol·L^{-1}), acquisition time 1.64 s, delay time 200 s, number of scans 1149. $AgNO_3$ (5.9 M in D_2O) was used as external reference.

^{252}Californium plasma desorption time-of-flight mass spectrometry (^{252}Cf PDMS)[13] experiments were carried out on a Bio/Ion 20 plasma desorption mass spectrometer. IR spectra of KBr pellets were measured on a Perkin-Elmer 283 spectrophotometer. For both UV and CD measurements, methanol of spectroscopic grade was used as solvent. UV and CD spectra of (5Me)Th-Met-Histam ($c = 6.8 \times 10^{-5}$ mol·L^{-1}; $\epsilon_{294} = 1.5 \times 10^4$, $\epsilon_{263} = 9.5 \times 10^3$ L·mol^{-1}·cm^{-1}) and [Ag{(5Me)Th-Met-Histam}](OTf) ($c = 7.5 \times 10^{-5}$ mol·L^{-1}; $\epsilon_{300} = 1.4 \times 10^4$, $\epsilon_{266} = 1.1 \times 10^4$ L·mol^{-1}·cm^{-1}) were recorded on Perkin-Elmer LAMBDA 5 UV/vis and Jobin-Yvon M III spectrophotometers, respectively.

Methanol of p.a. grade was used as solvent in the following solution studies. Optical rotation was measured on a Zeiss Kreisspolarimeter at 293 K, λ = 589 nm, and l = 2 dm. Vapor pressure osmometry (VPO)

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(10) Due to extensive charge delocalization, trifluoromethanesulfonate or $O_3SCF_3^-$, shortened to triflate or OTf^-, is a very weak donor. When strong donor functions are present, this particular anion is unlikely to coordinate to a metal ion.

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Table I

a. Crystallographic Data for $[C_{16}H_{22}N_4S_2Ag]^+[O_3SCF_3]^- \cdot CH_3OH$

formula	$C_{17}H_{22}F_3N_4O_3S_3Ag \cdot CH_4O$
space group	$P2_12_12_1$
a, Å	11.339(1)
b, Å	13.122(1)
c, Å	17.451(1)
V, Å^3	2596.5(3)
Z	4
fw	639.46
temp, K	100
λ, Å	0.710 73 (Zr-filtered Mo Kα)
ρ_{calcd}, cm^{-3}	1.636
μ, cm^{-1}	10.5
R^a	0.037
$R_w{}^b$	0.043

b. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms of $([Ag\{(5Me)Th\text{-}Met\text{-}Histam\}]^+)_\infty$

atom	x/a	y/b	z/c	U_{eq},^{c}
Ag1	0.48387 (3)	0.24356 (3)	0.41073 (2)	0.0188 (1)
S1	0.6113 (1)	0.0772 (1)	0.3177 (1)	0.0245 (5)
S2	0.8202 (1)	0.3327 (1)	0.66721 (9)	0.0220 (4)
O1	0.4193 (4)	0.2665 (3)	0.5507 (2)	0.025 (1)
N1	0.0851 (4)	0.1118 (3)	0.5868 (3)	0.020 (1)
N2	0.1295 (5)	−0.0449 (4)	0.5536 (3)	0.023 (2)
N3	0.4034 (4)	0.1646 (4)	0.6548 (3)	0.019 (2)
N4	0.5616 (4)	0.1101 (4)	0.4878 (3)	0.020 (1)
C1	0.0674 (7)	0.0401 (5)	0.5356 (4)	0.024 (2)
C2	0.1870 (6)	−0.0262 (5)	0.6212 (4)	0.027 (2)
C3	0.1610 (5)	0.0718 (5)	0.6414 (3)	0.020 (2)
C4	0.2051 (5)	0.1316 (5)	0.7074 (3)	0.020 (2)
C5	0.2974 (5)	0.2119 (4)	0.6847 (4)	0.019 (2)
C6	0.4547 (5)	0.1943 (4)	0.5898 (4)	0.021 (2)
C7	0.5683 (6)	0.1386 (5)	0.5680 (3)	0.019 (2)
C8	0.5872 (6)	0.0189 (5)	0.4688 (4)	0.021 (2)
C9	0.5954 (6)	−0.0114 (5)	0.3897 (4)	0.026 (2)
C10	0.5950 (7)	−0.1088 (5)	0.3596 (4)	0.034 (2)
C11	0.6076 (7)	−0.1094 (6)	0.2797 (5)	0.037 (2)
C12	0.6186 (6)	−0.0160 (5)	0.2481 (4)	0.029 (2)
C13	0.6393 (7)	0.0148 (7)	0.1661 (4)	0.040 (3)
C14	0.6738 (6)	0.2118 (5)	0.5767 (4)	0.023 (2)
C15	0.6883 (5)	0.2542 (6)	0.6563 (3)	0.025 (2)
C16	0.7813 (6)	0.4446 (5)	0.6120 (4)	0.031 (2)

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] U_{eq} (Å^2) = $^1/_3$ of the trace of the orthogonalized U tensor.

measurements were carried out with a Knauer apparatus, calibrated with azobenzene prior to use. Since the stability of the instrument requires a substantial difference between experimental and room temperature, the VPO measurements were carried out at 318 K.

Conductivity measurements were done with a Consort K720 digital conductometer and a cell calibrated prior to use with freshly prepared KCl solutions. Because the reported limiting conductivity value of the Ag(I) cation $\lambda_{Ag}{}^0$ = 50.3 S·cm^{-1}·mol^{-1} was measured at 303 K,[14] all experiments were carried out at this temperature. The limiting conductivity of $O_3SCF_3^-$, $\lambda_{OTf}{}^0$, and the molecular complexity of $Ag^IO_3SCF_3$, A_{AgOTf}, were calculated from the Onsager limiting law, $\Lambda_e = \Lambda_0 - A(C_{eq})^{1/2}$ [Λ_e ≡ experimentally determined conductivity; C_{eq} ≡ equivalent concentration], and the Kohlrausch equation, $\Lambda_0 = \lambda_+{}^0 + \lambda_-{}^0$. The measured conductivities of AgOTf at three concentrations (2.01×10^{-1}, 1.61×10^{-2}, and 1.61×10^{-3} mol·L^{-1}) resulted in A_{AgOTf} = 86.88 S·cm^{-1}·mol$^{-3/2}$ and $\Lambda_{AgOTf}{}^0$ = 88.74 S·cm^{-1}·mol^{-1}. Hence $\lambda_{OTf}{}^0$ = 38.44 S·cm^{-1}·mol^{-1}.

X-ray Structure Determination. Pertinent data are given in Table Ia. Reflections (3369) with 1.2° < θ < 27.5° were collected for a block-shaped, ivory-colored crystal [0.42 × 0.42 × 0.48 mm] mounted on a glass fiber at 100 K on an Enraf-Nonius CAD4 diffractometer with Zr filtered Mo Kα radiation (λ = 0.71073 Å). [$\Delta\omega$ = 0.60 + 0.35 (tan θ)°; $\omega/2\theta$ scan; h, 0–14; k, 0–17; l 0–22]. Data were corrected for Lp and a small linear decay of 3%, but not for absorption. The structure was solved by standard Patterson and Fourier methods (SHELXS-86)[15] and refined on F by full-matrix least-squares methods (SHELX-76)[16] to a final R value of 0.037 [R_w = 0.043, $w^{-1} = \sigma^2(F)$, S = 1.78, 371 parameters] for 2827 observed reflections with $I > 2.5\sigma(I)$. Hydrogen atoms were located from a difference map and their positions refined (except for those of the methyl groups that were introduced at calculated positions and refined with fixed geometry) with four common isotropic thermal parameters. A final difference map did not show any features outside the range −0.68 to 0.75 e Å^{-3}. Both enantiomorphic structures were refined; the one with the lowest R value corresponds to the absolute S configuration of the ligand used (see Figure 1). Fractional atomic coordinates and thermal parameters are given in Table Ib. Scattering factors were taken from ref 17 and corrected for anomalous dispersion.[18] The programs PLATON and PLUTON[19] were used for geometrical calculations and illustrations. All calculations were carried out on a micro-VAX cluster.

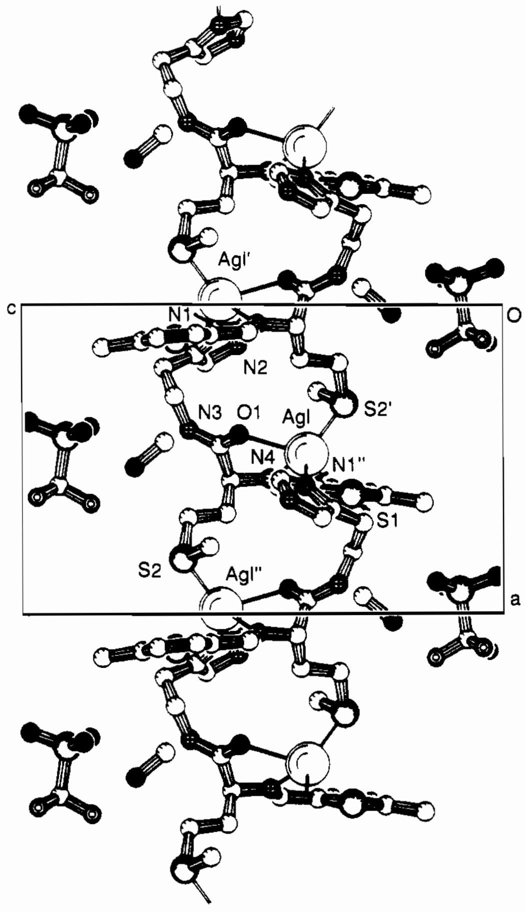

Figure 2. Projection down the b-axis of part of the absolute structure of $([Ag\{(5Me)Th\text{-}Met\text{-}Histam\}]^+[OTf]^- \cdot MeOH)_\infty$. ORTEP projections are available as Supplementary Material.

Results

From equimolar mixtures of the neutral donor ligand (5R)-Th-Met-Histam (R = H, Me, Me_3Si) with $Ag^IO_3SCF_3$ in methanol or with $Cu^IO_3SCF_3 \cdot {}^1/_2C_6H_6$ in benzene are obtained complexes with 1:1 ligand-to-metal stoichiometries. The off-white Ag(I) compounds are air-stable and are soluble in methanol, ethanol, and acetonitrile. Their solubility is very temperature dependent. The maximum concentration of [Ag{(5Me)Th-Met-Histam}](OTf) in methanol at 298 K lies on the order of 0.2 mol·L^{-1}; higher concentrations can be obtained but, eventually, result in crystallization. In solution, the Ag(I) complexes are moderately light sensitive and decompose after several hours of exposure to daylight. The orange/yellow Cu(I) complexes are very oxygen sensitive and can only be handled and stored under an inert atmosphere.

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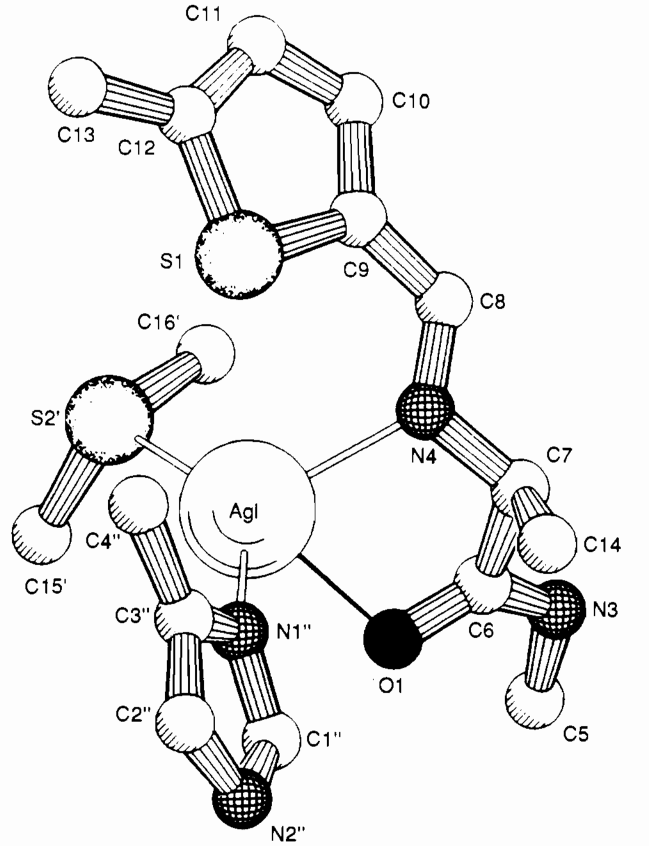

Figure 3. Coordination geometry of the Ag(I) centers in ([Ag{(5Me)-Th-Met-Histam}]$^+$[OTf]$^-$·MeOH)$_\infty$ and the adopted numbering scheme.

Solid-State Structure of [M{(5R)Th-Met-Histam}](OTf). The crystal structure of the 1:1 complex of (5Me)Th-Met-Histam and AgOTf, which was crystallized from a mixture of methanol, diethyl ether, and hexane, is shown in Figure 2. The adopted numbering scheme is shown in full in Figure 3. Distances and angles are given in Table II.

The structure consists of polymeric chains that are a result of the fact that each ligand stretches out over three different Ag(I) cations, in such a way that all Ag(I) centers are identically coordinated by three ligand molecules. These polymer chains exclusively possess a Δ-helix structure.[20] The triflate anions, which (as intended) do not coordinate to the metal centers, and methanol molecules (which are part of the crystal structure) are engaged in a repeating hydrogen-bonding interaction perpendicular to the helical axis. This interaction comprises bonding of an amide H with a methanol O, a methanol H with a triflate O, and another triflate O with an imidazole H^1 of a translated polymer. Since each ligand participates in two of these interchain connections (in two different directions), all polymer chains are linked to one another. The unique coordination geometry of the silver center is depicted in more detail in Figure 3.

The imine N4, methionine S2′, and imidazole N1″ atoms have the closest contacts with the Ag(I) cations, the distances being 2.378 (5), 2.509 (2), and 2.218 (4) Å, respectively. The three donor atoms and the Ag center constitute an almost perfect plane; the sum of the three interbond angles is 359.3°. Amide O1 is situated above this plane, though not directly over the silver atom, its relatively long distance of 2.568 (4) Å from the metal atom implying a weak bond. Thiophene S1 is located on the other side of the plane; however, the Ag–S distance of 3.081 (2) Å is too long to be considered a bond.[21] The configuration around each Ag(I) center in the N,S,N′ plane when observed along a perpendicular axis from S1 to O1 is *R*. As found in comparable Ag(I) complexes, the thienylmethylidene unit is planar (N4–C8–C9–S1: 18.0 (9)°), with an s–cis conformation, and the C=N function has the *E* configuration.[7,8] The amide group possesses the normal[22] trans configuration (O1–C6–N3–H8: −178 (7)°).

Table II. Selected Distances (Å) and Angles (deg) for ([Ag{(5Me)Th-Met-Histam}]$^+$)$_\infty$[a]

Ag1··Ag1′	6.471 (7)	Ag1′··Ag1··Ag1″	122.35 (1)
Ag1··S1	3.081 (2)	S2′–Ag1–O1	110.58 (11)
Ag1–S2′	2.509 (2)	S2′–Ag1–N1″	137.26 (13)
Ag1–O1	2.568 (4)	S2′–Ag1–N4	106.69 (13)
Ag1–N1″	2.218 (4)	O1–Ag1–N1″	91.65 (16)
Ag1–N4	2.378 (5)	O1–Ag1–N4	69.75 (15)
S1–C9	1.722 (7)	N1″–Ag1–N4	115.30 (17)
S1–C12	1.725 (7)	C9–S1–C12	92.3 (3)
S2–C15	1.826 (7)	C15–S2–C16	101.73 (3)
S2–C16	1.811 (7)	C1–N1–C3	106.9 (5)
O1–C6	1.235 (7)	C1–N2–C2	107.4 (5)
N1–C1	1.313 (8)	C5–N3–C6	122.9 (5)
N1–C3	1.387 (7)	C7–N4–C8	118.7 (6)
N2–C1	1.356 (9)	N1–C1–N2	110.6 (6)
N2–C2	1.370 (9)	N2–C2–C3	106.7 (6)
N3–C5	1.450 (8)	N1–C3–C2	108.2 (5)
N3–C6	1.333 (8)	N1–C3–C4	122.9 (5)
N4–C7	1.451 (7)	C2–C3–C4	128.8 (6)
N4–C8	1.275 (8)	C3–C4–C5	113.1 (5)
C2–C3	1.366 (9)	C4–C5–N3	111.3 (5)
C3–C4	1.481 (8)	O1–C6–C7	120.2 (6)
C4–C5	1.537 (8)	O1–C6–N3	123.6 (5)
C6–C7	1.529 (9)	C7–C6–N3	116.1 (5)
C7–C14	1.542 (9)	N4–C7–C6	108.6 (5)
C8–C9	1.440 (10)	N4–C7–C14	107.2 (5)
C9–C10	1.382 (9)	C6–C7–C14	109.4 (5)
C10–C11	1.402 (11)	N4–C8–C9	121.5 (6)
C11–C12	1.350 (10)	C8–C9–S1	121.4 (5)
C12–C13	1.505 (10)	C8–C9–C10	128.3 (6)
C14–C15	1.505 (9)	S1–C9–C10	110.3 (5)
		C9–C10–C11	112.5 (6)
		C10–C11–C12	114.3 (7)
		S1–C12–C11	110.6 (6)
		S1–C12–C13	119.1 (5)
		C11–C12–C13	130.3 (7)
		C7–C14–C15	113.9 (5)
		S2–C15–C14	113.2 (4)

[a] Symmetry operations by the screw axis are denoted by a single prime ($-^1/_2 + x$, $^1/_2 - y$, $1 - z$) and a double prime ($^1/_2 + x$, $^1/_2 - y$, $1 - z$), respectively.

Table III. Infrared Data[a] (cm^{-1}) for (5R)Th-Met-Histam and [Ag{(5R)Th-Met-Histam}](OTf)

	(5R)Th-Met-Histam		[Ag{(5R)Th-Met-Histam}](OTf)		
R	ν(C=N)	ν(C=O)	ν(C=N)	ν(C=O)	ν(S—O)
H	1628 s	1673 s	1622 s	1660 s	1027 vs 1255[b] vs; 1278[b] s
Me	1628 s	1670 s	1618 s	1663 s	1027 vs 1250[b] vs; 1280[b] s
Me$_3$Si	1630 s	1672 s	1618 s	1663 s	1025 vs 1250[b] vs; 1278[b] s

[a] KBr pellets. [b] Broad absorption.

Crystals of [Cu{(5Me$_3$Si)Th-Met-Histam}](OTf), crystallized from the same solvent mixture as the Ag(I) complex, were not suitable for X-ray structure elucidation. However, it could be established that its structure also has incorporated solvent molecules, since drying in vacuo afforded an amorphous powder.

A ^{252}Cf PDMS spectrum of dried, amorphous [Ag{(5Me)Th-Met-Histam}](OTf) does not show any clear peaks beyond m/z 800. Only a broad hump was observed in the range m/z 2500–5500. This result is most likely attributable to thermic fragmentation of high molecular aggregates and is consistent with an initially polymeric structure. In the lower range (apart from

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(20) The helix can be visualized by following the chain Ag–Imidazole–C$_\beta$–C$_\alpha$–CO–N–C$_\alpha$–C=N- -Ag–Imidazole– etc. (Figure 2).

(21) Maximum bond length = 1.59 Å (covalent radius of Ag) + covalent radius of the donor + 0.40 Å (usual tolerance); donor radii are as follows: S, 1.02 Å; N, 0.68 Å; O, 0.68 Å. *Manual*; Cambridge Crystallographic Data Base: Cambridge, U. K., 1988.

(22) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: New York, 1960; p 498.

Table IV. ^1H and ^{19}F NMR Data for (5R)Th-Met-Histam and [Ag{(5R)Th-Met-Histam}](OTf)[a]

		(5H)Th-Met-Histam			(5Me)Th-Met-Histam			($5Me_3Si$)Th-Met-Histam		
subunit	function	L	AgL	CuL[b]	L	AgL	CuL[b]	L	AgL	CuL[b]
(5R)Th	5R	7.45 d	7.64 d	7.67	2.48 s	2.50 s	2.46	0.34 s	0.28 s	0.24
	H^4	7.11 dd	7.29 dd	7.15	6.78 d[c]	6.89 d	6.87	7.27 d	7.34 d	~7.3
	H^3	7.57 d	7.73 d	7.74	7.23 d	7.44 d	7.47	7.50 d	7.66 d	7.71
	H^{im}	8.40 s	8.65 s	8.58	8.26 s	8.51 s	8.42	8.42 s	8.64 s	8.61
Met	$C_\alpha H$	3.95 dd	4.20 t	4.37	3.90 dd	4.18 t	4.39	3.96 dd	4.23 t	4.47
	$C_\beta H_2$	2.05 m	2.16 m	~2.1	2.05 m	2.20 m	~2.2	2.08 m	2.25 m	~2.2
	$C_\gamma H_2$	2.38 m	2.35 A	2.50	2.38 m	2.58[d]	2.65	2.48 m	2.55 A	~2.8
			2.69 B						2.64 B	
	$C_\epsilon H_3$	2.02 s	2.31 s	2.16	2.01 s	2.24 s	2.10	2.04 s	2.23 s	2.18
Histam	$C_\alpha H_2$	3.50 t	3.58 A	3.76	3.49 t	3.53 A	3.64[e]	3.50 t	3.60 A	3.59
			3.93 B			3.67 B			3.76 B	
	$C_\beta H_2$	2.78 t	2.93 t	2.95	2.78 t	2.91 t	2.96	2.79 t	2.91 t	~2.8
	H^2	7.55 s	7.96 s	8.01	7.55 s[c]	7.87 s	7.94	7.57 s	7.85 s	~8.0
	H^5	6.83 s	7.12 s	7.12	6.83 s	7.09 s	7.10	6.85 s	7.10	~7.1
O_3SCF_3	^{19}F		−78.39	−78.10		−78.21	−78.18		−78.27	78.30

[a] 298 K, CD_3OD, δ in ppm relative to Me_4Si (^1H) or $CFCl_3$ (^{19}F), s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, and A/B = A or B part of an AB spin system. [b] The spectra of these Cu(I) complexes show peaks without resolved multiplicity. [c] An additional small coupling (<0.5 Hz) to a more distant ring proton is sometimes observable. [d] AB pattern not observed due to the high intensity of the 5R methyl singlet. [e] At 233 K this pattern consists of two separate peaks.

some low-intensity ligand-fragment peaks) the most significant peak is found at m/z 457.1, i.e. $[ML]^+$. The presence of this ion indicates that the aggregate structure(s) can be fragmented easily under the experimental conditions. At m/z 565.6 there is a low-intensity peak assigned to $[M_2L]^+$.

IR data (KBr pellets) for the dried, amorphous, silver(I) complexes are listed in Table III. Compared with the values measured for the free ligands, only small shifts [10 cm^{-1} (average)] to lower wave numbers are found for the amide I (predominant C=O character) and C=N frequencies.[23] While the lower energy S–O frequency is very sharp, the higher energy one is split into two, rather broad, overlapping peaks. These data indicate that the C_{3v} symmetry of the free triflate anion has been lowered,[24] most likely as a result of a hydrogen-bonding interaction of the oxygen atoms with the amide H atom of the (5R)Th-Met-Histam ligand.

Solution Structure of [M{(5R)Th-Met-Histam}](OTf). The ^{19}F NMR spectrum of each of the Ag(I) and Cu(I) complexes in CD_3OD at 298 K shows one singlet resonance. The chemical shifts (relative to $CFCl_3$, see Table IV), ranging from δ −78.2 to −78.4, indicate that the O_3SCF_3 anions do not coordinate to the metal center.[5a]

^1H-NMR data, obtained in CD_3OD at 298 K, are given in Table IV. Compared to the spectra of the free ligands, the spectra of the Ag(I) complexes show one set of signals that is shifted to lower field. Evident shift differences are found for the imine H (0.22–0.25 ppm), the thiophene H^3 (0.16–0.21 ppm), the imidazole H^2 and H^5 (0.32–0.41 and 0.25–0.29 ppm, respectively), and the methionine methyl H atoms (0.19–0.29 ppm). There is also a pattern change for the histamine $C_\alpha H_2$ and methionine $C_\gamma H_2$ groups from an apparent A_2 to an AB spin system[25] upon complexation. Resonances of acidic protons, i.e., nitrogen-bound H atoms, are not visible in methanolic solutions as a result of exchange with the solvent's deuterium.[26]

Figure 4. ^1H NMR spectra of [Ag{(5Me)Th-Met-Histam}](OTf) [c = 0.11 mol·L^{-1}, in CD_3OD (#) at 233 K with added pyridine (*): (a) pure complex; (b) complex + 0.25 equiv of pyridine; (c) complex + 1.0 equiv of pyridine; (d) complex + 2.0 equiv of pyridine.

A NOESY spectrum of [Ag{(5Me)Th-Met-Histam}](OTf) at 298 K shows cross peaks for the imine H and methionine $C_\alpha H$ and for imine H and thiophene H^3 resonances that are absent in the corresponding COSY spectrum. These cross peaks, which represent through space interactions, show that on average the thienylmethylidene–amino fragment possesses a planar, s-cis

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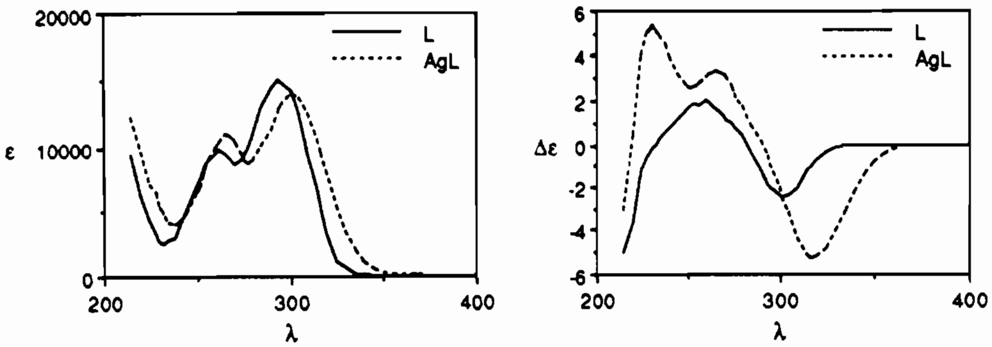
(23) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*; Methuen & Co., Ltd.: London, 1966; pp 203–205, 268–271.

(24) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. *Inorg. Chem.* **1982**, *21*, 969–977.

(25) Theoretically all prochiral CH_2 groups have an AB spin system, in the free ligand as well as the complexed ligand, due to the presence of the stereogenic center C_α of methionine. However at the magnetic field used (5.87 T), the diastereotopicity of the CH_2 protons is not necessarily evident. Coupling with ^{107}Ag and ^{109}Ag (both $I = {}^1/_2$) can be excluded as source of the pattern change because, for example, the singlet of methionine $C_\epsilon H_3$ is not affected. The AB character of the patterns was identified by irradiating the XY virtual triplet of histamine $C_\beta H_2$ and the multiplet of methionine $C_\beta H_2$.

(26) In CD_3CN, the amide H appears at δ 7.10 as a doublet of doublets, due to coupling with histamine $C_\alpha H_2$.



5a, UV plot

5b, CD plot

Figure 5. UV and CD plot for (5Me)Th-Met-Histam, L, and [Ag{(5Me)Th-Met-Histam}](OTf), AgL.

S=C—C=N conformation and an *E* C=N configuration, identical to that found in the solid state structure (vide supra).

Variation of the solution sample temperature in the range 328–183 K does not noticeably change the ^1H resonance frequencies, but the appearance of the spectra of the Ag(I) complexes is prominently affected by an increasing symmetric signal broadening[27] with decreasing temperature. This broadening, which is completely reversible, is already noticeable at 273 K (at high concentrations even at 298 K) and eventually results in a complete collapse of the ligand signals at 203 K. This behavior cannot be explained by increased solvent viscosity, since the signals associated with CD_3OD remain sharp, even at 203 K. An example of this low-temperature broadening is given by the spectrum of [Ag{(5Me)Th-Met-Histam}](OTf) at 233 K (c = 0.11 mol·L^{-1}) shown in Figure 4a. To examine the influence of additional donor ligands, pyridine was then added to this CD_3OD solution. As can be seen in Figure 4b–d, the chemical shifts of (5Me)Th-Met-Histam are not affected, yet the broadening decreases markedly with increasing pyridine concentration. The chemical shifts of the pyridine are identical to the values measured without a metal ion being present.

Because the ^1H NMR spectra signals of the Cu(I) complexes are broad even at 298 K, they yield less detailed information than that obtained for the corresponding Ag(I) complexes. It is unlikely that this broadening is caused by traces of Cu(II), since, in solution, the intense green of the oxidized complex, i.e., Cu(II), is easily distinguishable from the orange color of the Cu(I) complex. However, the signal patterns are distinct enough to confirm the same trends as found for the Ag(I) complexes, i.e., a marked downfield shift of the Cu(I) complexes' ^1H resonances compared to those of the free ligands. Moreover, at 233 K, two separate peaks are observed for the histamine $C_\alpha H_2$ group of the [Cu{(5Me)Th-Met-Histam}](OTf) complex.

^{109}Ag NMR data of Ag(I) complexes having ligands that only contain thienylmethylidene–amines as functional groups[7,8] have been easily obtained by the INEPT (insensitive nuclei enhanced by polarization transfer) pulse sequence,[28] with use of the ^3J-($^{107,109}Ag$–^1H) present on the imine H resonance. In their proton NMR spectra, complexes of the [Ag{(5R)Th-Met-Histam}](OTf) type do not, however, exhibit any resolved ^1H–Ag coupling. Therefore, only direct measurement of ^{109}Ag is available, and this is a very insensitive and time-consuming technique compared to INEPT. After numerous attempts a singlet ^{109}Ag resonance at δ 581 was detected for a clear saturated solution of [Ag{(5Me)-Th-Met-Histam}](OTf) (c = 0.3 mol·L^{-1}).

To investigate the solution structure of the [M{(5R)Th-Met-Histam}](OTf) complexes in more detail, [Ag{(5Me)Th-Met-Histam}](OTf) was extensively studied by a number of other techniques. The choice of this particular compound as a representative example was motivated by the possibility of correlating the results with the crystal structures of both the complex (vide infra) and the free ligand (5Me)Th-Met-Histam.[9]

The UV spectra of solutions of [Ag{(5Me)Th-Met-Histam}](OTf) and the free ligand (AgL and L, respectively; see Figure 5a) show quite comparable absorptions for the thienylmethylidene–amino chromophore.[28] The presence of the "chiral probe"[29] methionine C_α allows CD measurements. CD spectra of the same solutions (Figure 5b) show small Cotton effects, as is to be expected for an intrinsically symmetric chromophore whose electronic states are perturbed by dissymmetry elsewhere in the molecule.[30] Interestingly, the ligand and complex spectra are distinctly different: the complex (AgL) spectrum has a Cotton effect that is approximately twice the ligand's and exhibits an additional absorption maximum at λ = 225 nm.

The strong temperature dependence of the solubility of this complex already suggests that its solution structure is not based on simple, discrete units. More convincing evidence to support this idea of larger aggregates in solution comes from optical rotation measurements. The optical rotation value of solutions of the free ligand (5Me)Th-Met-Histam is concentration independent.[9] In contrast, [Ag{(5Me)Th-Met-Histam}](OTf) has a molar rotation that increases with concentration: a concentration of 1.54 × 10^{-2} mol·L^{-1} gives α^{20} of −39.0° L·mol^{-1}·dm^{-1}, whereas with a concentration of 7.72 × 10^{-2} mol·L^{-1} α^{20} is 50.5° L·mol^{-1}·dm^{-1}.

The increase of the complex's molar rotation with increasing concentration clearly indicates that some stereoregular association takes place; i.e., there is formation of an oligomeric species whose average chain length depends on the concentration.

Determination of the Average Chain Length. To establish the aggregation state of [Ag{(5Me)Th-Met-Histam}](OTf), or [AgL](OTf), in solution, vapor pressure osmometry (VPO) measurements (MeOH, 318 K) were carried out. The VPO data yield a number-average molecular weight, M_n, which is nonlinearly concentration dependent and ranges from $M_n \approx 300$ for infinitely dilute solutions to $M_n \approx 900$ for infinitely concentrated ones. A 10% w/w solution of the complex (c = 0.14 mol·L^{-1}, the same order of concentration as used for the ^1H NMR experiments) results in $M_n \approx 800$.

The lower limit of $M_n \approx 300$, almost exactly half of the calculated mass of the basic building block [AgL](OTf) (M_{calc} = 607.4) corresponds to the expected low concentration situation of two separate species, i.e., $[AgL]^+$ cations and OTf^- anions. The upper limit of $M_n \approx 900$ needs some explanation. The Ag(I) complex is not a mononuclear entity, yet even the limit situation of one infinitely large polycationic, polymeric, aggregate $([AgL]^+)_\infty$ and an infinite number of free OTf^- anions only results in a value

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(27) Linewidths ≥ 0.5 Hz are called "broad".

(28) Brevard, C.; van Stein, G. C.; van Koten, G. *J. Am. Chem. Soc.* **1981**, *103*, 6746–6748.

(29) The molecule 5-Me-Th-2-CH=N-*i*-Pr and its corresponding Ag(I) complex (discussed in ref 8) yield UV spectra with a practically identical pattern and trend, indicating that the spectra of Figure 5a are primarily attributable to absorptions of the thienylmethylidene–amino chromophore.

(30) Shanzer, A.; Yakirevitch, P.; Gottlieb, H.; Tor, Y.; Libman, J. *Pure Appl. Chem.* **1990**, *62*, 1111–1114.

(31) Crabbé, P. *Optical Rotary Dispersion and Circular Dichroism in Organic Chemistry*; Holden-Day; San Francisco, CA, 1965; pp 13–14.

of $M_n \approx M_{calc} = 607.4$. Therefore, at high concentrations there has to be cation–anion association. The equation relating the average oligomeric chain length, i, and the experimental value of the number-average molecular weight is given by

$$M_n = iM_{calc}/(1 + i\alpha_d)$$

where α_d is the degree of anion dissociation,[32] which has a value of 1 at infinite dilution. If we take the case of an infinite polymer, $i = \infty$, then at the high concentration limit where $M_n \approx 900$ (n.b. at 318 K) α_d is calculated to have a value of 0.67. N.b., the concentration dependence of α_d and i, is not likely to be linear, and since α_d and i are both independent variables, it is not possible to obtain their values at a given concentration by VPO alone. An approach to the estimation of α_d is to determine i by conductivity. For a 10% w/w solution of [AgL](OTf) (vide supra), the conductivity, Λ_e, at that specific concentration was measured and found to be 25.34 S·cm^{-1}·L·mol^{-1} (at 303 K).

In the model we are using there is a complexation/decomplexation process (k_1/k_{-1}) of n Ag(I) cations and n ligand molecules, yielding n basic building blocks $[AgL]^+$ (transient species) which polymerize in associative/dissociative processes (k_x/k_{-x}) to n/i oligomers with an average chain length i. See eq 1.

$$nAg^+ + nL \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left[n[AgL]^+\right] \underset{k_{-x}}{\overset{k_x}{\rightleftharpoons}} (n/i)([AgL]^+)_i \qquad (1)$$

In our case of multifunctional coordination, the complexed state is thermodynamically preferred, and $k_1 \gg k_{-1}$.

If one assumes that the complex polycations are oligomers that do not contribute significantly to the solution conductivity because they move too slowly (especially at higher concentrations this is not an unreasonable assumption) then the Onsager limiting law and Kohlrausch equation[14] now relate the experimental conductivity, Λ_e, and the desired degree of anion dissociation α_d according to

$$\alpha_d = \Lambda_e/(\lambda_{OTf}{}^0 - A^{AgL\cdot OTf}(C_{OTf})^{1/2})$$

in which $A^{AgL\cdot OTf}$ is the electronic interaction of the triflate anions with the complexed Ag(I) cations. In the present case a numerical calculation of this term is not feasible,[43] but by simply neglecting it (usually only allowed at low concentrations),[44] the measured value of Λ_e (25.34 S·cm^{-1}·L·mol^{-1}) at a concentration of 0.14 mol·L^{-1} yields a minimum value for $\alpha_d{}^{303}$ of 0.66. Consequently, $\alpha_d{}^{318}$ at this concentration, expected to be slightly larger than $\alpha_d{}^{303}$ value,[45] is close to the limiting value of 0.67 calculated from the M_n value of 900 (from VPO) combined with $i = \infty$. Hence, the measured M_n value of $\approx$800 at a concentration of 0.14 mol·L^{-1} gives an average chain length, i, of $\approx$ 11, i.e., 5.5 connected unit cells as depicted in Figure 2.

Discussion

There are several coordination complexes of Ag(I) cations with polydentate ligands that have polymeric solid-state structures.[33] However, to the best of our knowledge, there is only one documented example of such a complex that has a stereoregular helix structure comparable to that of ([Ag{(5Me)Th-Met-Histam)}][OTf]·MeOH)$_\infty$ described here, viz. (Ag{cyclo(L-methionyl-L-methionine)}[ClO$_4$])$_\infty$ described by Kojima and coworkers.[34] In the latter complex the ligand has two stereogenic centers and the X-ray structure shows each Ag(I) to be linearly coordinated by two thioether sulfur atoms of separate ligands; the silver center interacts additionally with four oxygen atoms of ClO_4^- anions.

Data relating to the solution structures of polymeric coordination complexes that can be directly compared with that presented here are scarce. Although there are solution structure studies of Ag(I) complexes with methionine and its derivatives, the majority of these data relate to charged, rather than neutral, ligand systems.[35] One study of possible relevance to the structure of [Cu{(5R)Th-Met-Histam}](OTf) is that of Whelan and Bosnich who reported that Cu(I) coordination complexes with a quadridentate ligand, supplying imidazole and thioether binding sites, may have a polymeric structure.[36]

The implications of the present results obtained for [M^I-{(5R)Th-Met-Histam}](OTf) (M = Ag, Cu) complexes are discussed separately for the two metals.

Solid-State Structure of [Ag{(5R)Th-Met-Histam}](OTf). The basic feature of the Ag(I) coordination geometry in the ([Ag-{(5Me)Th-Met-Histam}]$^+$[OTf]$^-$·MeOH)$_\infty$ X-ray structure is the plane formed by the Ag(I) center and its closest donor atoms: imine N4, imidazole N1, and methionine S2. Although the distances from these donor atoms to the metal center are well within their accepted bonding ranges,[21] they are considerably longer than those reported for linearly hybridized Ag(I) geometries. For example, the Ag–N4 distance of 2.378 (5) Å is 10% longer than the 2.16 Å (average) we have found in Ag(I) complexes containing only thienylmethylidene–amino functional groups.[7,8] In the Ag–N1 distance of 2.218 (4) Å this lengthening is less pronounced, but this bond is still noticeably longer than those in [Ag{imidazole}$_2$](X) complexes; 2.09 Å (average) (X = ClO$_4$)[37] and 2.12 Å (average) (X = NO$_3$)[38] Å. Finally, the Ag–S2 distance of 2.509 (2) Å is much longer than the 2.40 Å (average) found in the complex of Kojima et al. (vide supra).[34] Nevertheless, the predominantly trigonal surrounding in [Ag{(5R)Th-Met-Histam}](OTf) is best described in terms of an sp^2-hybridized Ag(I) ion with the lengthened bonds most likely reflecting a compromise between steric demands of the ligand and the bonding restraints associated with a planar Ag,N,N′,S arrangement.

Situated above this trigonal coordination plane is the amide O1 atom, which only has a weak interaction with the empty p-orbital of the Ag ion; this is evidenced by the long Ag–O distance of 2.568 (4) Å and the displacement of O1 from the ideal position directly over the metal center. The driving force of the bidentate coordination of the O1–C6–C7–N4 fragment of {(5R)Th-Met-Histam} is formation of the N4–Ag bond and not the O1–Ag interaction; generally, one requires, as here, chelate ring formation to induce the weakly basic amide O atom to bond to a metal cation.[39]

The presence of the thiophene S1 atom on the other side of the trigonal plane is also consequence of the N4–Ag bond. The E

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(45) It would be preferable to carry out all experiments at the same temperature but, unfortunately, VPO apparatus limitations prevent reliable measurements at 303 K (the temperature at which the limiting conductivity of $O_3SCF_3^-$ is known). Likewise, it would be interesting to follow the chirality–temperature dependence of a 10% w/w complex concentration by CD spectroscopy. However like UV measurements, CD measurements can only be carried out on in the absorption range of $0.2 < A < 2$, and this limits their application to low concentrations.

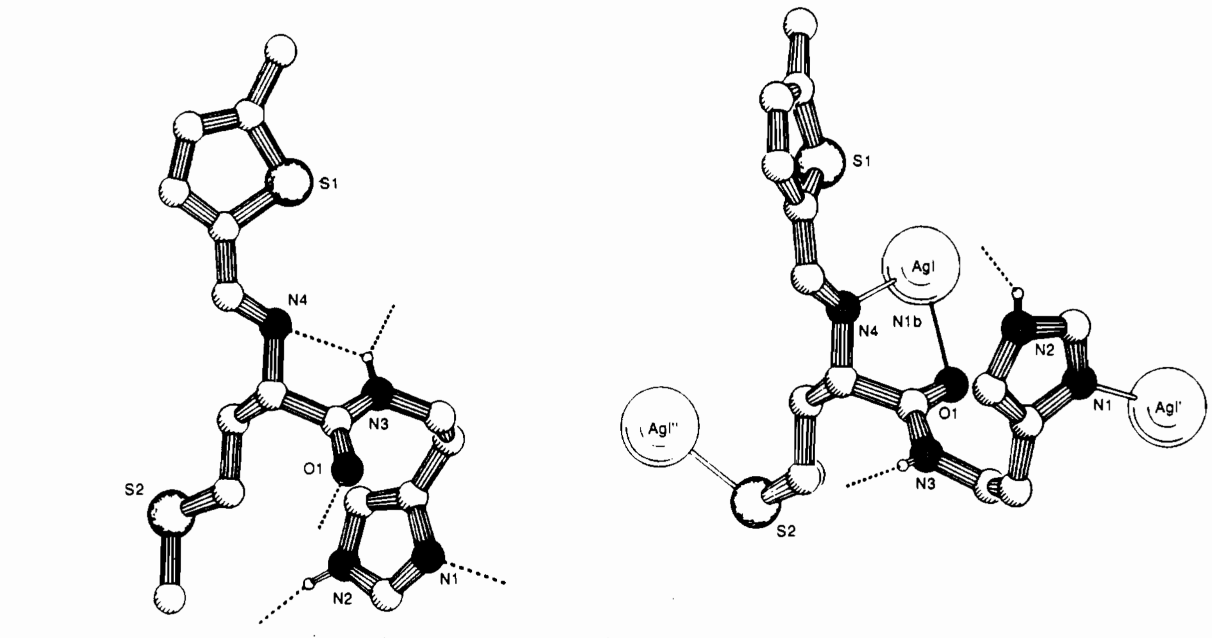

Figure 6. (5Me)Th-Met-Histam and [Ag{(5Me)Th-Met-Histam}]$^+$ compared (identical orientations at methionine C_α = C7).

Table V. Comparison between Relevant Dihedral Angles (deg) of (5Me)Th-Met-Histam, L, and ([Ag{(5Me)Th-Met-Histam}]$^+$[OTf]$^-$·MeOH)$_\infty$, AgL

function	chain	L	AgL	Δ^a
Histam	N1–C3–C4–C5	−74.5 (4)	−72.9 (7)	1.6
	C3–C4–C5–N3	−67.1 (4)	−64.4 (7)	3.3
	C4–C5–N3–C6	113.2 (4)	131.6 (6)	18.4
	C7–C6–N3–C5	−174.8 (3)	178.0 (5)	−7.2
	O1–C6–N3–H[N3]	−170 (3)	−178 (7)	−8
(5Me)Th	C7–N4–C8–C9	177.4 (3)	−172.8 (6)	9.8
	N4–C8–C9–S1	−12.2 (5)	18.0 (9)	30.2
Met	C7–C14–C15–S2	170.0 (2)	175.5 (5)	5.5
	C14–C15–S2–C16	−175.8 (3)	70.7 (5)	113.5
C_α (C7)	N3–C6–C7–N4	−37.4 (4)	133.2 (6)	170.6
	N3–C6–C7–C14	83.9 (4)	−110.1 (6)	166.0
	N4–C7–C14–C15	178.8 (3)	176.2 (5)	−2.6
	C14–C7–N4–C8	79.4 (4)	110.3 (6)	30.9

^{a} Δ ≡ smallest possible angle of rotation to turn the value of L into that of AgL.

Table VI. Overview of the Donor–Acceptor Combinations in (5Me)Th-Met-Histam, L, and ([Ag{(5Me)Th-Met-Histam}]$^+$[OTf]$^-$·MeOH)$_\infty$, AgL

donor–acceptor	L	AgL
N4 imine	H[N3] amide	Ag
O1 amide	H'[N3'] amide	Ag
H[N3] amide	N4 imine & O1' amide	O MeOH
N1 imidazole	H'[N2'] imidazole	Ag
H[N2] imidazole	N1' imidazole	O OTf
S2 methionine		Ag

configuration of the imine function combined with the resonance stabilized planarity of the thienylmethylidene–amino unit will favour an s-cis N4═C8—C9═S1 conformation[8] which brings the thiophene S and Ag atoms together. However, no actual bond is formed, as evidenced by the long Ag–S1 distance of 3.081 (2) Å, though some dipole–cation attraction cannot be excluded. (See ref 8 for a detailed discussion.)

In this silver complex each molecule of (5Me)Th-Met-Histam contributes as a ligand to the coordination geometry of three separate Ag(I) centers and contributes in such a way that a coordination polymer results. Therefore, it is worthwhile to compare the solid-state structures of (5Me)Th-Met-Histam both as the free molecule[9] (Figure 6) and as a ligand coordinated to Ag(I). It is striking that the (5Me)Th-Met-Histam moieties in these two situations have nearly identical bond lengths (maximum difference 0.034 Å) and bond angles (maximum difference less than 5° but typically less than 2°). Only some dihedral angles, summarized in Table V, have changed markedly upon complexation.

In the Ag(I) complex the basic shapes of the three arms of (5Me)Th-Met-Histam (see Introduction) are not dramatically altered relative to those of the free molecule: (i) The "histamine–amide" subunit retains its gauche conformation, but there are some small changes, notably a rotation of 18.4° about the C5–N3 bond. (ii) In the thienylmethylidene–amino fragment there is a rotation of 30.2° about the C8–C9 bond. This change of dihedral angle along the C8–C9 bond is most likely due to a stacking effect in the complex that results in a thiophene ring system which is oriented almost perpendicular to the direction of the polymeric chain. The planarity of the thienylmethylidene function and, hence, the resonance stabilization through π-conjugation[40] is hardly affected by this rotation. (iii) The dihedral angles of the methionine side chain indicate that the all-trans conformation of the free ligand is, to a large extent, conserved in the complex. Only the position of the terminal methyl group has changed markedly as a result of a rotation of 113.5° about the C15–S2 bond. We tentatively propose that the driving force of this rotation might be a decrease this gives in projection of the methyl group out of the polymeric cylinder.

In the complex the dihedral angles around the stereogenic carbon center C7 show that relative orientations of these three arms are, however, substantially altered as a result of a half-circle rotation of the entire "histamine-amide" subunit about C6–C7. This conformational change of the (5Me)Th-Met-Histam molecule upon complexation has a simple explanation. The shape of the uncomplexed molecule is most probably governed by a tendency to pair all of the donor and acceptor functions present (see Table VI). This results in a bifurcated hydrogen-bonding mode of the amide H atom H[N_3], interacting intramolecularly with imine N4 and intermolecularly with amide O1', that determines the orientation at C6–C7. These donor–acceptor combinations are disrupted by Ag(I) cations since the donor functions prefer to coordinate to these much stronger Lewis acids. This then allows rotation about C6–C7, and the three arms of the ligand can reorientate, giving the ligand a more rodlike shape, so that amide O1 can approach the metal atom, which is coordinated by imine N4.

Apart from the rotation about C6–C7 all other changes upon complexation are rather small. Except for the thioether sulfur, which does not participate in hydrogen bonding, all Lewis acid and base functions in free (5Me)Th-Met-Histam and its Ag(I) complex are involved in bonding interactions (Table VI). Since polymer formation occurs in a completely stereoregular way (yielding only Δ helices), the stereoselectivity must arise from the single stereogenic carbon center C7, i.e., methionine C_α.

Solution Structure of [Ag{(5R)Th-Met-Histam}](OTf). With the working hypothesis that the solution structure of [Ag{(5R)-Th-Met-Histam}](OTf) is likely to be related to that in the solid, one can concentrate on answering two interrelated questions: (i) which groups constitute the coordination geometry of the metal cation in solution, and (ii) what is the aggregation state? Both questions will be dealt with here in that order. The chemical shift range of the ^{19}F NMR data (Table IV) clearly indicates that, as intended, the triflate anions do not coordinate to the Ag(I) cations.

The downfield shifts and pattern changes in the ambient-temperature ^{1}H NMR spectra of [Ag{(5R)Th-Met-Histam}](OTf) upon addition of AgOTf (Table IV) are evidence for a thermodynamically stable coordination complex. The downfield shifts of the protons in the thienylmethylidene–amino moiety indicate coordination of the imine N atom to a Ag(I) center, and this, together with the E configuration of the C=N bond and its coplanar s-cis conformation with respect to the thiophene ring (established by a NOESY experiment), brings the thiophene S atom into the metal's proximity.[8] The imidazole H atoms exhibit even larger downfield shifts, consistent with coordination of the N^3 atom to a Ag(I) center. The downfield shift of the methionine $C_\epsilon H_3$ singlet shows that the thioether S atom coordinates to a metal cation. The pattern changes observed for the histamine $C_\alpha H_2$ and methionine $C_\gamma H_2$, from A_2 to AB, reflect a spatial fixation of these aliphatic chain parts that is consistent with amide O and thioether S atom coordination.

The ^{109}Ag chemical shift of δ 581 measured for a solution of the [Ag{(5Me)Th-Met-Histam}](OTf) complex, being in the transition range between pure linearly coordinated (<500 ppm) and tetrahedrally coordinated (>600 ppm) silver,[41] is in agreement with the presence of a trigonally coordinated Ag(I) cation.

At all temperatures, the ^{1}H NMR spectra only show one set of signals, indicating that all ligands form complexes in the same way and that complexation is stereoselective. The CD data support this conclusion. Since the electronic states of the thienylmethylidene–amino chromophore in free (5Me)Th-Met-Histam and its corresponding Ag(I) complex are similar (as evidenced by their UV spectra, Figure 5a), one can make valid comparisons of their CD spectra (Figure 5b). The marked increase of the Cotton effect upon addition of 1 equiv of Ag(I) cations to free (5Me)Th-Met-Histam is a clear indication that a stable coordination product has been obtained with a predominant handedness.[42]

In summary, these results agree well with a solution Ag(I) geometry that is comparable to the solid-state geometry, i.e., a metal center surrounded by amide O, thiophene S, imidazole N, imine N, and methionine S atoms in a single configuration, with predominantly trigonal coordination by the latter three donor atoms.

Bearing in mind the 1:1 metal-to-ligand stoichiometry and the fact that there is only one ligand identity on the NMR time scale, one can deduce, a priori, that the aggregation state that allows this specific Ag(I) geometry is based on either discrete (as opposed to averaged) mono-, di-, and trication complexes or a polycationic species with the same repeating unit as the solid-state structure. Vapor pressure osmometry (VPO) measurements are consistent with an oligomeric structure where the number-average molecular weight M_n obtained can be explained by association–dissociation of the triflate anions to and from the oligomeric chains. The chemical shift range of $\delta(^{19}\text{F})$ is evidence that this exchange process does not occur at the metal center, and one can therefore conclude that association–dissociation in solution takes place at the amide H atoms; this interaction is established for both the crystal and amorphous structure of the complex.

The knowledge gained thus far about the character of the complexes, permits a plausible explanation of the phenomena observed in the ^{1}H NMR spectra at various temperatures. The kinetic processes in solution which determine the appearance of the ^{1}H NMR spectra are the association/dissociation of oligomeric chains (eq 1: k_x/k_{-x}) and conformational changes in the oligomers; the (de)complexation process (eq 1: k_1/k_{-1}) cannot be important as it involves the unlikely situation of simultaneous breaking of the coordination bonds with three different ligands.[5] Thus at ambient temperatures the sharp ^{1}H NMR signals indicate a fast exchange situation for the former processes. The increasing and symmetric signal broadening found upon lowering the probe temperature (≤273 K) cannot be attributed to intermediate exchange phenomena since it affects all peaks at the same time. Instead, this broadening must be attributed to chemical shift anisotropy (CSA), resulting from a decrease in the tumbling rate and, hence, of the spin–spin relaxation time constant T_2. When tumbling rates noticeably affect the appearance of ^{1}H NMR spectra at relatively high temperatures, as here, one has good evidence for the presence of macromolecular structures.[46] At 200 K the increased contribution of CSA culminates in a complete collapse of all signals. At the onset of the broadening there is still a fast exchange situation, and unfortunately, this domination of CSA prevents the detection of possible intermediate or slow exchange phenomena at lower temperatures. This interpretation of the line-shape phenomena is supported by the pyridine addition experiment at 233 K (Figure 4). The chemical shift positions of neither the (5Me)Th-Met-Histam ligand nor pyridine change when the two species are mixed, and thus the N-donor pyridine ligand does not affect the thermodynamic stability of the original coordination compound. However, since the (5Me)Th-Met-Histam ligand signals become sharper, one can conclude that pyridine is competing with the multifunctional ligand for the silver cations; the decrease of CSA with increasing pyridine concentration is consistent with a decrease in the average oligomeric chain length.

Structure of [Cu$^{\text{I}}${(5R)Th-Met-Histam}](OTf). No crystal structure determination of a representative of the studied [Cu{(5R)Th-Met-Histam}](OTf) complexes could be carried out. The observation that tiny crystals of one Cu(I) compound turned amorphous when dried in vacuo suggests incorporation of solvent, most likely MeOH, as is found in the crystal structure of [Ag{(5Me)Th-Met-Histam}](OTf).

The highly similar trends in the ^{1}H and ^{19}F NMR data of the AgOTf and CuOTf complexes with {(5R)Th-Met-Histam} (Table IV) make it legitimate to assume that the basic solution structures of the two series of coordination complexes are identical. The subtle differences in ^{1}H chemical shifts positions between the two series probably reflect small differences in the coordination affinities of the donor functions to the two different metal centers. The marked broadening of the Cu(I) complex ^{1}H NMR signals over the whole temperature range (318–188 K) is less easily explained.

Casella suggested that the broad signals found for his Cu(I) coordination complex is attributable to the quadrupole moment of the copper nucleus.[47] This is unlikely to apply here; the Cu(I) complex [Cu{5-Me-Th-2-CH=N-*i*-Pr}$_2$](OTf) has very sharp ^{1}H NMR signals over a large temperature range.[8]

It would be tempting to ascribe this broadening in the proton NMR spectra of [Cu{(5R)Th-Met-Histam}](OTf) to intermediate exchange phenomena that are occurring at higher temperatures than for corresponding Ag(I) complexes; the smaller ionic radius of Cu(I) is expected to afford more tightly bonded complexes. However, although this explanation is likely to be true in complexes with easily adaptable ligand systems,[5] it may not apply in this particular case where the ligand imposes a coordination geometry on the metal center. More importantly, the signals of the Cu(I) complex do not collapse at low temperatures and the pattern of the histamine $C_\alpha H_2$ group does not change from A_2 to AB until the temperature is lowered to 233 K. This behavior is not consistent with an intermediate exchange situation at ambient temperatures.

In our opinion the broadening of the signals which dominates the ^{1}H NMR spectra of the Cu(I) complexes at all temperatures

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is related to the presence of the imidazole function. This proposal can be used not only to explain the aforementioned results of Casella and the findings in this paper, but also the broadened signals in the ^{1}H NMR spectra (298 K) of $[Cu(I)\{imidazole\text{-}4\text{-}CH_2SR\}_2]^+$ complex cations for which intermediate exchange processes can be excluded.[48] As a possible explanation we suggest that in copper(I) imidazole complexes there is an equilibrium involving an intramolecular metal-to-ligand electron shift, i.e., between diamagnetic Cu(I)–imidazole and paramagnetic Cu(II)–imidazole$^{\bullet-}$.[49] Although such an equilibrium can lie far to the side of Cu(I), a small population of the other state can be sufficient to cause extensive line broadening in the NMR spectra. The electron shift equilibrium might facilitate Cu(I)/Cu(II) redox transitions, this perhaps being the reason that nature favors imidazole (over pyridine, pyrazole, or whatever N atom donor) as a coordinating function for copper ions.

Conclusions

Coordination complexes from 1:1 metal salt to ligand reactions of $Ag^IO_3SCF_3$ and the polydentate donor ligand system *N*-[*N*-((5-R-thienyl)methylidene)-L-methionyl]histamine (=(5R)Th-Met-Histam; R = H, Me, Me_3Si) possess intriguing helical polycationic structures, both in the solid state and in solution. The origin of the self-organization relates to the specific structure of the (5R)Th-Met-Histam molecule, which, as a result of steric constraints and the number, nature, and partitioning of its donor and acceptor functions, is preorganized to coordinate to three different Ag(I) cations.

A noteworthy aspect of the complex structure is its complete stereoregularity that is induced by the ligand's single stereogenic carbon center. The corresponding Cu(I) complexes are isostructural to their Ag(I) counterparts. In addition to the oligoligand approach,[3,4] the present self-assembly mechanism provides a second option for the preparation of polycationic coordination complexes.

Acknowledgment. The Netherlands Foundation for Chemical Research (SON) and the Netherlands Organization for Scientific Research (NWO) are thanked for financial support. We gratefully acknowledge the assistance of Prof. Dr. N. M. M. Nibbering and R. Fokkens concerning the ^{252}Cf-PDMS experiment and of Dr. H. P. J. M. Dekkers (University of Leiden) with the CD measurements. Thanks are also due to J.-M. Ernsting for recording the 250-MHz ^{1}H NMR spectra, to A. J. M. Duisenberg for X-ray data collection, to Dr. C. J. Elsevier for helpful discussions, and to Dr. D. M. Grove for his careful reading of the manuscript.

Registry No. ($[Ag\{(5Me)Th\text{-}Met\text{-}Histam\}]^+[OTf]^-MeOH$), 124781-00-6; $[Ag\{(5Me)Th\text{-}Met\text{-}Histam\}](OTf)$, 124780-99-0; $[Ag\{(5H)Th\text{-}Met\text{-}Histam\}](OTf)$, 139100-67-7; $[Ag\{(5Me_3Si)Th\text{-}Met\text{-}Histam\}](OTf)$, 139100-69-9; $[Cu\{(5H)Th\text{-}Met\text{-}Histam\}](OTf)$, 139100-71-3; $[Cu\{(5Me)Th\text{-}Met\text{-}Histam\}](OTf)$, 139100-73-5; $[Cu\{(5Me_3Si)Th\text{-}Met\text{-}Histam\}](OTf)$, 139100-75-7; ^{109}Ag, 14378-38-2.

Supplementary Material Available: Three ORTEP plots (50% probability) and tables giving refined parameters, bond distances, bond angles, and thermal motion parameters (8 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Protonation of a Metal–Metal Bond Can Lead to Bond Shortening

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Received October 16, 1991

The complex $[CoRh(CO)_3(\mu\text{-dppm})_2]$ (**1**) is easily protonated to give $[CoRh(\mu\text{-H})(CO)_3(\mu\text{-dppm})_2]^+$ (**2**). The structure of **2**$[BF_4]$ has been determined crystallographically [space group $P\bar{1}$, $a = 12.673$ (2) Å, $b = 19.833$ (3) Å, $c = 11.992$ (3) Å, $\alpha = 94.29$ (2)°, $\beta = 117.08$ (2)°, $\gamma = 107.93$ (1)°, $Z = 2$, $R = 0.0519$, $R_w = 0.0558$] and it is shown that the Co–Rh bond is shorter in **2** than in **1**. This is the first example of such a bond shortening on protonation of a metal–metal bond and reasons for the unique behavior are discussed. Complex **2** exhibits fluxionality in solution and it is suggested that this occurs by inversion of the CoRh(μ-H) unit.

Introduction

Protonation of a metal–metal bond has been thought always to lead to an increase in metal–metal bond distance. For example, early work showed that the metal–metal distance in $[Cr_2(\mu\text{-H})(CO)_{10}]^-$ [3.406 (9) Å] was 0.44 Å longer than in $[Cr_2(CO)_{10}]^{2-}$ [2.97 (1) Å].[2] The same effect has been observed in several complexes bridged by bis(diphenylphosphino)methane and related ligands.[3] Thus, the metal–metal bond distance in $[RhRe(CO)_4(\mu\text{-dppm})_2]$ [2.7919 (6) Å] is 0.21 Å shorter than that in $[RhRe(\mu\text{-H})(CO)_4(\mu\text{-dppm})_2]^+$ [3.0036 (7) Å].[3] When protonated metal–metal distances are shorter than other metal–metal distances in the same molecule, there are other bridging groups in the MM′(μ-H)(μ-X) unit which cause the effect; that is, the bond-shortening effect of μ-X may outweigh the bond-lengthening effect of μ-H.[4] In these cases, it is presumed that deprotonation would lead to a still shorter metal–metal distance although good structural data for both protonated and deprotonated forms are lacking. The lengthening of a metal–metal bond upon protonation is expected in terms of conversion of a 2c–2e bond to a 3c–2e bond as depicted in eq 1.[4]

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