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COPPER(I), SILVER(I) AND ZINC(II) CATIONS IN MULTIFUNCTIONALIZED DONOR-ATOM ENVIRONMENTS COMPRISING TWO IMIDAZOLE N–, TWO THIOETHER S– AND TWO AMIDE O-ATOMS

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ABSTRACT. — Reactions of $M(n)(O_3SCF_3)_n$ salts [M(*n*) = Ag(I), Cu(I) or Zn(II)] and the N, S, O donor ligand N-[*n* + 1)-(5-methyl-4-imidazolyl)-*n*-thiaalkanoyl]benzylamine (*n*-thiaalkanoyl = 3-thiabutanoyl or 4-thiapentanoyl) in a M:L = 1:2 stoichiometry, give rise to formation of mononuclear ML_2 complexes. The tetrahedral metal coordination geometry comprises two imidazole N^3- and two thioether S-atoms [Ag(I), Cu(I)] or two imidazole N^3- and two amide O-atoms [Zn(II)].

These M:L = 1:2 coordination complexes are kinetically labile in solution: even at low temperatures (180 K) intramolecular, ligand site exchange processes are taking place.

Reactions of $M(n)(O_3SCF_3)_n$ salts [M(*n*) = Ag(I), Cu(I) or Zn(II)] and the N, N′, S, S′, O, O′ donor ligand N–[N–{(*n* + 1)–(5-methyl-4-imidazolyl)-*n*-thiaalkanoyl}-L-methionyl]histamine (*n*-thiaalkanoyl = 3-thiabutanoyl or 4-thiapentanoyl) in a M:L = 1:1 stoichiometry, produce (most likely stereoregularly formed) oligomeric complexes. These $(ML)_m$ polycationic chains are a result of the fact that each ligand stretches out over at least three metal nuclei, while all metal centres possess an identical coordination environment. Although only coordination of the imidazole N^3-atoms has been established with certainty, the tentative coordination geometries of the different cation types are very similar to those found in the M:L = 1:2 species.

Interpretation of the ^{1}H-NMR data of the Cu(I) complexes is difficult because of a prominent signal broadening. This signal broadening is ascribed to a paramagnetic relaxation by Cu(II), which is formed in an intramolecular electron shift equilibrium involving Cu(I)-imidazole and Cu(II)-imidazole$^{\cdot-}$ transitions.

Introduction

As part of a program to study the structural aspects of copper(I) and silver(I) coordination complexes with ligands, containing nitrogen and sulphur donor atoms [1], we have recently published the synthesis and structural characterization (by X-ray and NMR) of the M:L = 1:1 complex of $Ag(I)O_3SCF_3$ and the chiral, polydentate ligand N-[N-{5-methyl-2-thienylmethylidene}-L-methionyl]histamine (Figure 1; the ligand is abbreviated as (5Me)Th-Met-Histam) [2].

Due to the fact that (5Me)Th-Met-Histam stretches out over three separate Ag(I) centres, a coordination polymer is formed, which exclusively has a Δ-helix. Each Ag(I) nucleus is predominantly trigonally planar coordinated by an imidazole N–, an imine N– and a thioether S-atom, provided by the histamine, thienylmethylidene-amino and methionine subunits of three different ligands. There is also a weak coordination of an amide O-atom. The thiophene S-atom does not coordinate, although residing in the proximity of the Ag-atom due to the preferred ligand conformation. The solution structure of this Ag(I) and the corresponding Cu(I) complex is very similar, consisting of oligomers which have the same repetitive unit as the polymers found in the solid state. The fact that there are no dramatic changes in ligand structure upon coordination and, moreover, the complete stereoregularity of the polymerization, attributable to induction of the ligand's only stereogenic carbon centre methionine-C_α, represent a degree of self-organization [3], which is unprecedented in synthetic coordination chemistry.

Aiming to obtain a pure N_2S_2 coordination of Cu(I) and Ag(I) cations, a logical development involved substitution of the thienylmethylidene-amino moiety of (5Me)Th-Met-Histam by an imidazole N– and thioether S-atom donating fragment [4]. As a promising candidate, the 4-imidazolylmethylidenesulfide function was selected [5]. Based on the latter function, a novel class of ligands was synthesized, comprising molecules of the N-{N-[*n* + 1)-(5-methyl-4-imidazolyl)-*n*-thiaalkanoyl]-L-methionyl}histamine type, in which the *n*-thiaalkanoyl fragment is either 3-thiabutanoyl or 4-(thiapentanoyl (abbreviated as (5Me) Im-SA-Met-Histam, with SA = SB or SP, respectively; Figure 2a) [6]. The (5Me)Im-SA-Met-Histam molecules are specifically designed to provide two imidazole-N and two thioether-S donor atoms, but they also contain two amide-O atoms, which might affect the ligand's coordination, as was established for the M:L = 1:1 Ag(I) complex of (5Me)Th-Met-Histam

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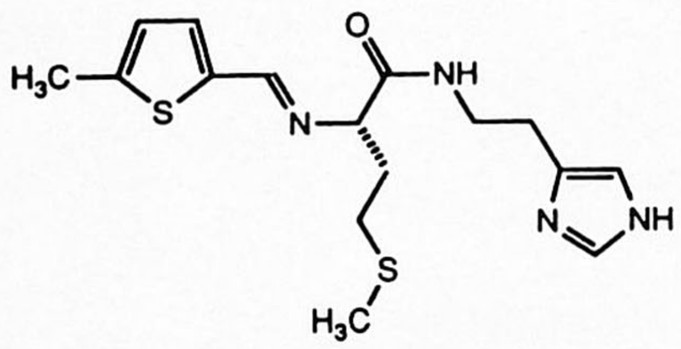
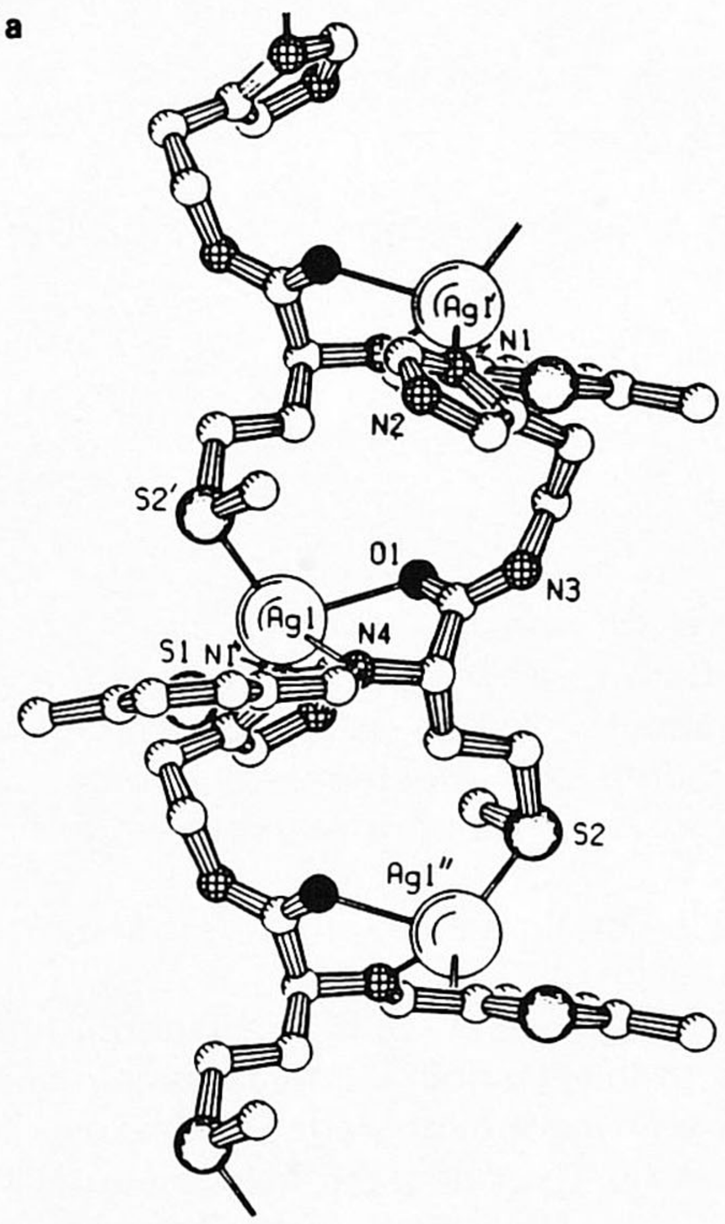
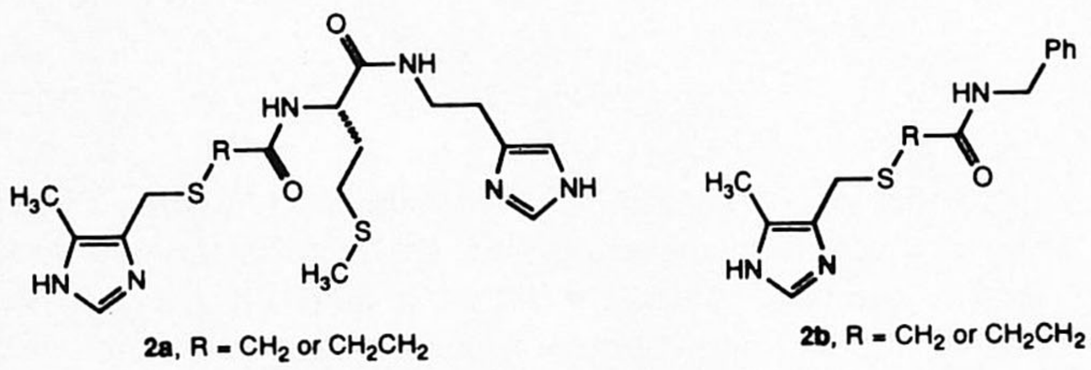


1a



1b

Figure 1. – (5Me)Th-Met-Histam, **1a**, and X-ray structure of its 1:1 Ag(I) complex, **1b**.



2a, R = CH_2 or CH_2CH_2 **2b**, R = CH_2 or CH_2CH_2

Figure 2. – (5Me)Im-SA-Met-Histam, **2a**, and (5Me)Im-SA-$NHCH_2$Ph, **2b**.
R = CH_2; SA = SB
R = CH_2CH_2; SA = SP

1b [2]. Hence, molecules of the **2a** type can be viewed as N, N′, S, S′, O, O′ donor ligands.

The possible contribution of amide-O coordination might influence the intended N, S binding mode of the 4-imidazolylmethylidenesulfide function. This prompted us to investigate also the coordination behaviour of the 4-imidazole-thiaalkanoyl containing building block separately, incorporated in N, S, O donor ligands of the N-[(n + 1)-(5-methyl-4-imidazolyl)-n-thiaalkanoyl]benzylamine type (abbreviated as (5Me)Im-SA-$NHCH_2$Ph; Figure 2b) [6]. As the (5Me)Im-SA-$NHCH_2$Ph ligands (**2b**) require a M:L = 1:2 stoichiometry to achieve a possible N_2S_2 coordination, they supply an (N, S, $O)_2$ donor set, and therefore can also serve as a model for the more complicated set built in (5Me)Im-SA-Met-Histam (**2d**).

This paper discusses the structures of coordination complexes formed by reacting Ag(I)O_3SCF_3 and Cu(I)O_3SCF_3 salts with either (5Me)Im-SA-Met-Histam or (5Me)Im-SA-$NHCH_2$Ph, in M:L stoichiometries of 1:1 and 1:2, respectively. Differences and similarities in the coordination behaviour of these same ligands towards the group 12 dication Zn(II), which like Ag(I) and Cu(I) has a d^{10} electronic configuration, might enhance the understanding of structural aspects in either complex type. Accordingly, Zn(II)$(O_3SCF_3)_2$ complexes of both (5Me)Im-SA-Met-Histam and (5Me)Im-SA-$NHCH_2$Ph have been prepared and their structural data will be correlated with the corresponding Ag(I) and Cu(I) complexes.

Experimental

PHYSICAL MEASUREMENTS

^{1}H-NMR and ^{19}F-NMR spectra of CD_3OD solutions were recorded on a Bruker WM250 spectrometer, tetramethylsilane being used as external reference, and a Bruker AC100 spectrometer, with $CFCl_3$ as external reference, respectively. Infrared data were measured on a Perkin Elmer 283 spectrophotometer as KBr pellets or on a Nicolet model 7199B FT-IR spectrophotometer as liquid films in methanol (AgCl windows, substraction of the methanol spectrum).

PREPARATION OF THE COMPOUNDS

Methanol and benzene were freshly distilled and stored under nitrogen.

The syntheses of N-[4-(5-methyl-4-imidazolyl)-3-thiabutanoyl]benzylamine [(5Me)Im-SB-$NHCH_2$Ph] and N-{N-[4-(5-methyl-4-imidazolyl)-3-thiabutanoyl]-L-methionyl}histamine [(5Me)Im-SB-Met-Histam] have been published [6], the corresponding 5-(5-methyl-4-imidazolyl)-4-thiapentanoyl derivatives, (5Me)Im-SP-$NHCH_2$Ph and (5Me)Im-SP-Met-Histam were prepared via the same procedure.

Copper(I) trifluoromethanesulfonate. $1/2C_6H_6$ (Cu(I)$O_3SCF_3.1/2C_6H_6$) was prepared as described by Salomon and Kochi [7].

Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, T.N.O., Zeist, The Netherlands.

All syntheses were carried out under an atmosphere of dry nitrogen. For each ligand type, the preparation of the complex with the butanoyl derived ligand will be described; the complexes of the corresponding pentanoyl derivatives were synthesized, following the same method. ^{1}H- and ^{19}F-NMR data of the free ligands and the complexes are given in Tables II and III.

[(5Me)Im-SA-$NHCH_2$Ph]Ag(I)O_3SCF_3 complexes

Solutions of 0.82 g (2.99 mmol) of (5Me)Im-SB-$NHCH_2$Ph in MeOH (10 mL) and 0.38 g (1.48 mmol) of Ag(I)O_3SCF_3 in MeOH (10 mL) were mixed. After 30 minutes, the resulting turbid solution was filtered. Subsequently, the solvent was distilled off under reduced pressure, yielding 1.14 g of [Ag{(5Me)Im-SB-$NHCH_2$Ph}$_2$](O_3SCF_3) (95%), as off-white solids. Analytical data, found (calc. for $C_{29}H_{34}AgF_3N_6O_5S_3$): C 43.53(43.12), H 4.22(4.25), F 7.05(7.06), N 10.30(10.40), S 11.51(11.91).

[Ag{(5Me)Im-SP-$NHCH_2$Ph}$_2$](O_3SCF_3), analytical data, found (calc. for $C_{31}H_{38}AgF_3N_6O_5S_3$): C 44.24(44.55), H 4.38(4.59), F 6.81 (6.82), N 10.02(10.06), S 11.43(11.51).

[(5Me)Im-SA-$NHCH_2$Ph]Cu(I)O_3SCF_3 complexes

A solution of 0.32 g (1.27 mmol) of Cu(I)$O_3SCF_3.1/2C_6H_6$ in benzene (25 mL), was added to a suspension of 0.70 g (2.55 mmol) of (5Me)Im-SB-$NHCH_2$Ph in benzene (15 mL). The resulting suspension was stirred for 1 h, during which a green, gum-like material precipitated. Subsequently, the solvent was decanted and the remaining sticky substance was dried in vacuo, yielding [Cu{(5Me)Im-SB-$NHCH_2$ Ph}$_2$](O_3SCF_3) as light green solids. Analytical data, found(calc.

for $C_{29}H_{34}CuF_3N_6O_5S_3$): C 46.46(45.63), H 4.45(4.49), F 8.00(7.47), N 10.13(11.03), S 11.95(12.60).

[Cu{(5Me)Im-SP-$NHCH_2Ph$}$_2$](O_3SCF_3), analytical data, found (calc. for $C_{31}H_{38}CuF_3N_6O_5S_3$): C 46.68(47.05), H 4.66(4.84), F 7.08 (7.20), N 10.34(10.62), S 11.89 (12.15).

[(5Me)Im-SA-$NHCH_2Ph$]Zn(II)(O_3SCF_3)$_2$ complexes

The off-white Zn(II)(O_3SCF_3)$_2$ complexes were obtained via the procedure described for the corresponding [(5Me)Im-SA-$NHCH_2$ Ph]Ag(I)O_3SCF_3 complexes (vide supra).

[Zn{(5Me)Im-SB-$NHCH_2Ph$}$_2$](O_3SCF_3)$_2$, analytical data, found (calc. for $C_{30}H_{34}F_6N_6O_8S_4Zn$): C 40.70(39.41), H 4.19(3.75), F 11.62 (12.47), N 8.91(9.19), S 13.27(14.03).

[Zn{(5Me)Im-SP-$NHCH_2Ph$}$_2$](O_3SCF_3)$_2$, analytical data, found (calc. for $C_{32}H_{38}F_6N_6O_8S_4Zn$): C 40.36(40.79), H 4.28(4.07), F 11.60 (12.10), N 8.82(8.92), S 13.15(13.61).

[(5Me)Im-SA-Met-Histam]Ag(I)O_3SCF_3 complexes

Methanolic solutions of 0.62 g (1.51 mmol) of (5Me)Im-SB-Met-Histam (10 mL) and 0.39 g (1.51 mmol) of Ag(I)O_3SCF_3 (10 mL) were mixed. After 30 minutes, the resulting turbid solution was filtered. Subsequently, the solvent was distilled off under reduced pressure, yielding 0.96 g of [Ag{(5Me)Im-SB-Met-Histam}](O_3SCF_3) (95%), as light yellow solids. Analytical data, found (calc. for $C_{18}H_{26}AgF_3N_6O_5S_3$): C 32.51(32.39), H 4.07(3.93), F 8.28(8.58), N 12.10(12.59), S 13.55(14.41).

[Ag{(5Me)Im-SP-Met-Histam}](O_3SCF_3), analytical data, found (calc. for $C_{19}H_{28}AgF_3N_6O_5S_3$: C 32.66(33.48), H 4.29(4.14), F 8.69 (8.36), N 11.55(12.33), S 13.72(13.11).

[(5Me)Im-SB-Met-Histam]Cu(I)O_3SCF_3 complexes

A solution of 0.39 g (1.55 mmol) of Cu(I)O_3SCF_3.1/2C_6H_6 in benzene (25 mL) was added to a suspension of 0.63 g (1.55 mmol) of (5Me)Im-SB-Met-Histam in benzene (15 mL). The resulting suspension was thoroughly stirred for 5 h, without any marked changes occurring. Subsequently, the solvent was filtered off and the remaining grey solids of [Cu{(5Me)Im-SB-Met-Histam}](O_3SCF_3) were dried in vacuo. Analytical data, found(calc. for $C_{18}H_{26}CuF_3N_6O_5S_3$): C 37.46(34.69), H 5.38(4.21), F 7.29(9.15), N 12.97(13.49), S 13.87(15.44).

[Cu{(5Me)Im-SP-Met-Histam}](O_3SCF_3) was synthesized accordingly, but no analytical data were obtained.

[(5Me)Im-SA-Met-Histam]Zn(II)(O_3SCF_3)$_2$ complexes

The light yellow Zn(II)(O_3SCF_3)$_2$ complexes were obtained via the procedure described for the corresponding (5Me)Im-SA-Met-Histam. Ag(I)O_3SCF_3 complexes (vide supra).

[Zn{(5Me)Im-SB-Met-Histam}](O_3SCF_3)$_2$, analytical data, found (calc. for $C_{19}H_{26}F_6N_6O_8S_4Zn$): C 28.63(29.48), H 3.66(3.39), F 14.13 (14.73), N 10.33(10.86), S 16.18(16.57).

[Zn{(5Me)Im-SP-Met-Histam}](O_3SCF_3)$_2$, analytical data, found (calc. for $C_{20}H_{28}F_6N_6O_8S_4Zn$): C 29.66(30.48), H 3.68(3.58), F 14.21 (14.46), N 9.89(10.66), S 15.58(16.27).

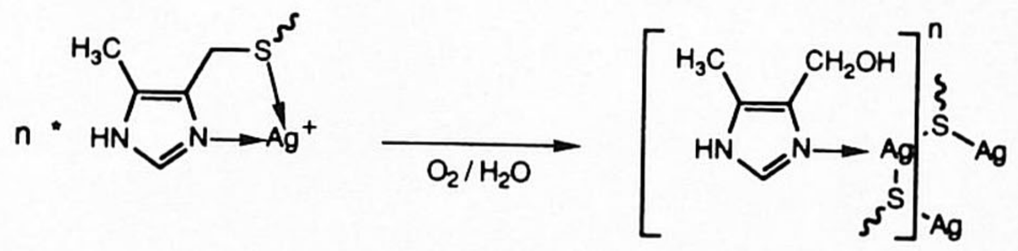
Results

SYNTHESIS OF THE COMPLEXES

Complexes were obtained by reacting the appropriate M(n)(O_3SCF_3)$_n$ salt and either two equivalents of (5Me)Im-SA-$NHCH_2Ph$ **2b** or one equivalent of (5Me)Im-SA-Met-Histam **2a** in methanol [M(n) = Ag(I) or Zn(II)] or benzene [M(n) = Cu(I)]. The isolated compounds, especially the Cu(I) complexes, are very oxygen sensitive, decomposing rapidly when exposed to air. The M:L = 1:2 complexes of **2b** are soluble in MeOH, EtOH and MeCN whereas their M:L = 1:1 counterparts of **2a** dissolve well in MeOH, moderately in EtOH and only slightly in MeCN.

Despite the use of an inert atmosphere as well as oxygen free solvents, solutions of the Cu(I) complexes decompose upon standing for prolonged periods (days).

Small amounts of white solids are formed upon mixing the Ag(I) or Zn(II) salt and **2a** or **2b** ligands. Heating up and/or deliberate addition of water to solutions of the complexes does increase the amount of insoluble product formed. However, once filtered and kept under inert atmosphere, solutions of Ag(I) and Zn(II) complexes are stable for weeks and, in case of Ag(I), only moderately light sensitive. Therefore, the insoluble white solids must be decomposition products. In analogy with the removal of thiolate protection groups like triphenylmethane by Ag(I) or Hg(II) cations [8], the mechanism of the present decomposition process most likely involves a heterolytical cleavage of the imidazolylmethylidenesulfide thioether bond by the Ag(I) or Zn(II) cations, catalyzed by traces of oxygen or water, resulting in a M^{n+}–S^- bond. Metal thiolates have commonly a low solubility due to a strong preference of the S^- function for bridge bonding, which leads to polynuclear or polymeric structures [9]. The proposed mechanism is illustrated schematically (for Ag) in Equation 1.



(1) (2)

Despite numerous attemps, no single crystals of the Ag(I), Cu(I) or Zn(II) complexes suitable for X-ray diffraction structure determination could be obtained. Cooling down of highly concentrated methanolic solutions and/or addition of apolar solvents, like diethyl ether, resulted at best in precipitation of waxy substances, which, after decantation of the solvent and drying in vacuo, had NMR characteristics identical to those of the product isolated directly, by distilling off the solvent.

The discrepancies in the found and calculated analytical data of the Cu(I) and Zn(II) complexes, are attributable to the presence of minor amounts of solvent, being benzene and MeOH, respectively. Benzene enclosed in solids is hard to remove completely at ambient temperatures, as evidenced by the fact that traces of this solvent are always visible in the ^{1}H-NMR spectra of the Cu(I) complexes. In case of the Zn(II) complexes, the persistence of MeOH may suggest a coordination to the metal nucleus, via an oxygen lone pair, as is frequently found for water molecules in zinc enzymes [10].

SPECTROSCOPIC DATA OF THE [M(n){**2b**}$_2$]$^{n+}$($O_3SCF_3^-$)$_n$ COMPLEXES

The wavenumber of the amide-I infrared absorption of the (5Me)Im-SA-$NHCH_2Ph$ ligand (Table I)[11], does not change markedly upon complexation to Ag(I) and only slightly in case of Cu(I). In the Zn(II) complexes, on the other hand, there is a substantial frequency decrease, 25-28 cm^{-1}, compared with the free ligands.

The found ^{19}F-NMR shift range of δ – 78.19 to – 78.39 ppm (Table II) indicates that, in solution, the $O_3SCF_3^-$ anions are not coordinated [12].

The room temperature H-NMR spectra of all M:L = 1:2 complexes show only one set of resonance patterns indicating that all (5Me)Im-SA-$NHCH_2Ph$ ligands are equal on the NMR

Table I. – Infrared data [a] of $\nu_{amide\text{-}I}$ [b] of (5Me)Im-SA-NHCH$_2$Ph, **L**, and [M(*n*){(5Me)Im-SA-NHCH$_2$Ph}$_2$]$^{n+}$($O_3SCF_3^-$)$_n$, **ML$_2$**.

Ligand	L	AgL_2	CuL_2	ZnL_2
(5Me)Im-SB-NHCH$_2$Ph	1650 (1652)	1650 (1653)	(1647)	1625
(5Me)Im-SP-NHCH$_2$Ph	1645	1645		1617

[a] 298 K, ν in cm^{-1}, measured as KBr pellets or in methanol (between brackets), all absorptions are (very) strong; [b] Reference 11.

time scale. The resonances (Table II) have shifted compared with the free ligand, indicating that cationic coordination complexes have been formed. In the ^{1}H-NMR spectra of the Cu(I) complexes, the signals are also slightly, but noticeably broadened [13]. After addition of extra ligand (implying the presence of more than 2 equivalents of ligand per metal ion), the spectra still show one pattern set but the shift differences become less prominent. The imidazole-H^2 resonance is the only one shifting substantially in the M:L = 1:2 complexes: up to 0.33 ppm to lower field. Apart from the $C_\alpha H_2$ resonance of the thiabutanoyl function (SB) in the Zn(II) complex, all other chemical shift changes are minimal.

Upon lowering the probe temperature to 223 K, a peak broadening [13] is observed for the signals of the M:L = 1:2 complexes, notably the resonances of the (5Me)Im-SA part. This broadening disappears again upon reheating (though not completely in case of the Cu(I) complexes, vide supra). Cooling further (ie < 213 K) the broadening increases, but no pattern changes occur even at the experimental limit temperature of ~ 185 K.

SPECTROSCOPIC DATA OF THE [M(n){2a}]$^{n+}$($O_3SCF_3^-$)$_n$ COMPLEXES

As expected, a ^{19}F chemical shift range of δ – 78.30 ppm (Table III) is found for the [M(*n*){(5Me)Im-SA-Met-Histam}$^{n+}$ ($O_3SCF_3^-$)$_n$ complexes, which indicates that, in solution, the $O_3SCF_3^-$ anions do not coordinate [12].

As in the ^{1}H-NMR spectra of the M:L = 1:2 complexes of **2b**, the spectra of the M:L = 1:1 complexes of **2a** show only one set of resonance patterns over the whole temperature range of 328–180 K, indicating that all ligands are equal on the NMR time scale. The room temperature ^{1}H-NMR data of the free and complexed (5Me)Im-SA-Met-Histam ligands (Table III), show substantial changes upon addition of the metal salt, indicating that cationic coordination complexes have been formed.

Table II. – ^{1}H- and ^{19}F-NMR data [a] of (5Me)Im-SA-NHCH$_2$Ph, **L**, and [M(n){(5Me)Im-SA-NHCH$_2$Ph}$_2$]$^{n+}$($O_3SCF_3^-$)$_n$, **ML$_2$**.

		(5Me)Im-SB-NHCH$_2$Ph				(5Me)Im-SP-NHCH$_2$Ph			
Subunit	Function	L	AgL_2	CuL_2 [b]	ZnL_2	L	AgL_2	CuL_2 [b]	ZnL_2
(5Me)Im	5-CH_3	2.12s	2.15s	2.15s	2.20s	2.17s	2.22s	2.23s	2.20s
	H^2	7.45s	7.76s	7.86s	7.68s	7.45s	7.75s	7.88s	7.83s
SA	$C_\alpha H_2$	3.15s	3.14s	3.15s	3.39s	2.48t	2.47t	2.50t	2.45t
	$C_\beta H_2$	—	—	—	—	2.67t	2.66t	2.70t	2.68t
	$C_{\delta/\varepsilon} H_2$	3.73s	3.79s	3.79s	3.81s	3.68s	3.74s	3.76s	3.74s
CH_2Ph	$C_\alpha H_2$	4.36s	4.28s	4.29s	4.36s	4.36s	4.30s	4.30s	4.37s
	C_6H_5	7.29s	7.25s	7.25s	7.25s	7.26s	7.25s	7.26s	7.26s
O_3SCF_3	^{19}F	—	–78.19s	–78.39s	–78.36s	—	–78.35s	–78.27s	–78.19s

[a] 298 K, CD_3OD, δ in ppm relative to Me_4Si (^{1}H) or $CFCl_3$ (^{19}F), s = singlet, t = triplet; [b] Unresolved multiplicity due to slightly broadened signals; the most probable interpretation is given.

Table III. – ^{1}H- and ^{19}F-NMR data [a] of (5Me)Im-SA-Met-Histam, **L**, and [M(n){(5Me)Im-SA-Met-Histam}]$^{n+}$($O_3SCF_3^-$)$_n$, **ML**.

		(5Me)Im-SB-Met-Histam				(5Me)Im-Sp-Met-Histam			
Subunit	Function	L	AgL	CuL [b]	ZnL	L	AgL	CuL [b]	ZnL
(5Me)Im	5-CH_3	2.17s	2.23s	[c]	2.23s	2.19s	2.24s	[c]	2.24s
	H^2	7.47s	7.82s	[c]	7.86s	7.48s	7.83s	[c]	8.00s
SA	$C_\alpha H_2$	3.15s	3.25s	~ 3.2	3.45 [d]	2.53t	2.55t [d]	~ 2.5	2.50t [d]
	$C_\beta H_2$	—	—	—	—	2.70t	2.75t [d]	~ 2.8	2.65t
	$C_{\delta/\varepsilon} H_2$	3.75s	3.89s	[c]	3.82AB	3.70s	3.78s	[c]	3.74AB
Met	$C_\alpha H$	4.42dd	4.36dd	4.40	4.34dd	4.41dd	4.40dd	4.44	4.36dd
	$C_\beta H_2$	1.85m	1.90m	1.90	1.90m	1.80m	1.85m	1.90	1.90m
	$C_\gamma H_2$	2.46m	2.50m	~ 2.5	2.40m	2.45m	2.50m [d]	~ 2.5	2.45m [d]
	$C_\varepsilon H_3$	2.05s	2.11s	2.07	2.02s	2.05s	2.12s	2.04	2.03s
Histam	$C_\alpha H_2$	3.44t	3.46m	3.45	3.45m [d]	3.42t	3.45m	3.45	3.44m
	$C_\beta H_2$	2.78t	2.86t	~ 2.8	2.84t	2.75t	2.80t [d]	~ 2.8	2.86t
	H^2	7.57s	7.87s	[c]	8.05s	7.58s	7.88s	[c]	8.05s
	H^5	6.84s	7.03s	[c]	7.06s	6.83s	7.02s	[c]	7.04s
O_3SCF_3	^{19}F	—	–78.30s	–78.29s	–78.23s	—	–78.24s	–78.24s	–78.27s

[a] 298 K, CD_3OD, δ in ppm relative to Me_4Si (^{1}H) or $CFCl_3$ (^{19}F), s = singlet, dd = doublet of doublets, t = triplet, m = multiplet, AB = AB pattern; [b] Unresolved multiplicity due to substantial peak broadening; [c] No observable peak at 298 K; at 253 K, however, a broad hump is visible, having a chemical shift close to the value found in the free ligand; [d] Exact multiplicity unclear due to coinciding patterns; where possible, the most probable interpretation is given.

The most profound changes are exhibited in the ^{1}H-NMR spectra of the Cu(I) complexes: the imidazole proton resonances and those of the protons of neighbouring groups are completely invisible while the remaining peaks are extensively broadened [13]. At lower temperatures (< 253 K), the missing peaks initially reappear, evidencing that the ligand is still intact, until all signals collapse completely at about 200 K. The present broadening is similar to, but even more prominent than the broadening found in the [Cu{(5Me)Th-Met-Histam}]$^+$ complex cation (see Introduction) [2b].

In the corresponding Ag(I) and Zn(II) complexes, the room temperature chemical shift positions and patterns have undergone marked changes compared with the free ligands. In both complexes, the imidazole proton resonances have shifted considerably [H^5 ~ 0.2 (Ag and Zn) and H^2 ~ 0.3 (Ag) to ≥ 0.4 (Zn) ppm] to low field, and in both cases the Histam-$C_\alpha H_2$ pattern has changed from a apparent triplet in the free ligand to a multiplet in the complex [14]. Other marked changes include (i) a downfield shift for the methionine-$C_\varepsilon H_3$ singlet of 0.06-0.07 in the Ag(I) complex and (ii) a pattern change for the SA-$C_{\delta/\varepsilon}H_2$ spin system from a singlet in the free ligand to an AB pattern in the Zn(II) complexes; coinciding peak patterns prevent the detection of a possible, similar change of the SA-$C_\alpha H_2$ resonances.

Interestingly, already at 273 K a broadening [13] occurs of all ^{1}H resonance patterns of the (5Me)Im-SA-Met-Histam ligand in the M:L = 1:1 Ag(I) and Zn(II) complexes; this broadening is reversible on reheating. Lowering the probe temperature further, the broadening increases sharply, culminating into a complete collapse of the signals at 213 K [Ag(I)] or 233 K [Zn(II)]. This trend is identical to that of the Ag(I) complex of (5Me)Th-Met-Histam, **1b**, in solution (see Introduction)[2b].

The broadening, observed for the Cu(I), Ag(I) and Zn(II) complex resonances does not affect the signals associated with the solvent [15].

Discussion

As shown by various crystal structures of Cu(II) complexes, the N,S donating function 4-imidazolylmethylidenesulfide (abbreviated to Im-SR) coordinates in a chelating fashion [16] its N^3–C–C–S conformation barely changing upon complexation [17].

The "hard-soft acid base" theory (HSAB) [18] predicts that imidazole N^3- and thioether S-atoms bind the group 11 monocations Cu(I) and Ag(I) even better than the dication Cu(II), hence a priori a similar chelating coordination is expected for the former metal centres, provided no additional steric constraints are present [7]. The ^{1}H-NMR data of a Cu(I) complex in which Im-SR is part of the ligand, support an N,S chelating binding mode [5].

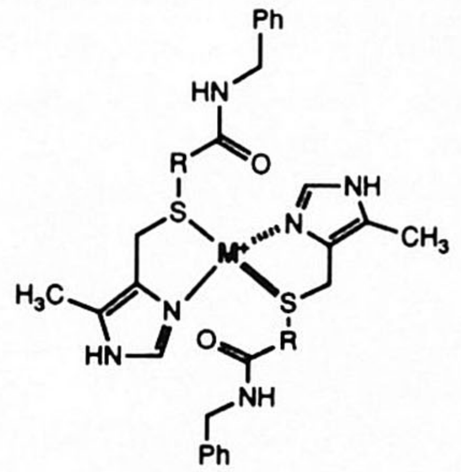
In the case of the group 12 dication Zn(II), the HSAB theory [18] predicts that Im-SR will coordinate strongly via the imidazole N^3-atom, but at best only weakly via the thioether S-atom. Indeed, ^{1}H-NMR data of Zn(II) complexes with Im-SR containing ligands only clearly reflect a Zn–N bond, but nevertheless the simultaneous presence of a (weak) Zn–S bond is proposed [5]. However, the latter interpretation seems somewhat doubtful in relation to an X-ray structure of a Zn(II) complex with a ligand having a comparable N,S moiety, that does not reveal any Zn–S interaction [20].

Obviously, it is rather difficult to establish the actual structures of the complexes with the (Im-SR containing) ligands **2a** and **2b** without X-ray data. Yet, based on a combination of experimental data (mainly derived from NMR experiments) and literature data, a plausible structure can be postulated.

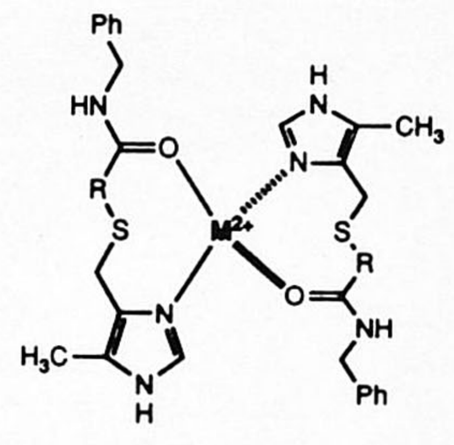
STRUCTURE OF THE $[M(n)\{\mathbf{2b}\}_2]^{n+}(O_3SCF_3^-)_n$ COMPLEXES

In addition to the N,S donating function Im-SR, the (5Me)Im-SA-$NHCH_2Ph$ ligands **2b** incorporate the amide O-atom as an additional potential donor site. According to HSAB theory [18], Ag(I) and Cu(I) at best bind weakly with this function (cf. the X-ray structure of the Ag(I) complex of (5Me)Th-Met-Histam, **1b** [2]. In the M:L = 1:2 Ag(I) and Cu(I) complexes of (5Me)Im-SA-$NHCH_2Ph$, however, there are enough strong N and S donor atoms available to satisfy the highest possible coordination number of the group 11 monocations, ie four [21], hence no actual M(I)-O bond is expected. Bearing in mind that Ag(I) and Cu(I) do not favour a square planar coordination geometry [21], the most likely structure of these M:L = 1:2 complexes consists of a tetrahedrally N_2S_2 coordinated M(I) cation, as shown in Figure 3a.

While the amide O-atom in unlikely to affect the coordination geometry of the group II monocationic complexes, it is more than likely to be present in the Zn(II) coordination sphere, since HSAB theory [18] predicts Zn(II) to interact strongly with any oxygen donor. Although Zn(II) can accommodate up to six donors, its metal coordination sphere in the M:L = 1:2 complexes is most likely an N_2O_2 dominated tetrahedron [22]; yet some contribution of a Zn- thioether-S bond cannot a priori be ruled out. Because a chelating binding mode of the (5Me)Im-SA-$NHCH_2Ph$ ligand is less inevitable with N,O than with N,S coordination, the resulting hypothetical structure may either be a mononuclear (Fig. 3b) or a binuclear complex cation.



3a, R = CH_2 or CH_2CH_2, M^+ = Ag(I) or Cu(I)



3b, R = CH_2 or CH_2CH_2, M^{2+} = Zn(II)

Figure 3. – Schematic representations of the expected coordination geometries (Λ configuration shown) [23].

The ^{1}H-NMR data of the M:L = 1:2 complex cations, exhibit a marked shift of the imidazole-H_2 resonance, indicating coordination of imidazole-N_3 to the metal centre [2].

Infrared spectroscopy (IR) proves a useful tool in establishing coordination of other donors. Assuming a similar coordination geometry in the solid state and in solution (cf. the absorptions of the Ag(I) complexes, Table I), the amide-I absorption frequencies are rather informative. Bearing in mind that this absorption possesses a predominant C=O character [11], the nearly identical wavenumbers of free and complexed ligand indicate that amide-O coordination to Ag(I) or Cu(I) is extremely weak to nonexistent. However, the substantial energy decrease upon addition of Zn(II), clearly suggest that the amide O-atom does coordinate to this metal dication.

The phenomena observed in the variable temperature ^{1}H-NMR spectra of all M:L =1:2 complexes can be rationalized on bases of the postulated tetrahedral coordination geometries. At room temperature the complexes are prone to fast intermolecular exchange processes (cf. the experiments with excess ligand, vide supra), involving ligand association/dissociation. Lowering the temperature, the intermolecular exchange processes are

interrupted as the imidazole-N^3-metal bond becomes stable on the NMR time scale, but intramolecular exchange processes (ligand site exchange) are still taking place. The onset of signal broadening at ~ 220 K can be explained by the Ω, λ inversion process [23] of the tetrahedral coordination geometry. Only in that case, a slowing down of the intramolecular exchange processes on the NMR time scale (an intermediate exchange situation) results in a observable asymmetry of the metal configuration through a broadening of the resonances of the ligands prochiral groups [24]. Even at the lowest possible temperatures, however, a slow exchange situation, i.e. a stable chelating coordination, cannot be achieved in solution as evidenced by the fact that no complete decoalescence occurs of the prochiral resonances. Therefore, the resulting structures are extremely flexible in solution.

Because only imidazole-N^3 coordination is actually established for Ag(I) and Cu(I), their coordination geometries may be pseudo-tetrahedral, ie a linear N_2 coordination with restricted rotations about the M(I)-N bond [1d]. However, taking into account the preferred N_3-C–C–S conformation of the Im-SR fragment, as a result of which the S-atom resides in proximity of the M(I) centre [17], and the high affinity of both Ag(I) and Cu(I) for thioether sulphur [18], a pure N_2S_2 coordination is highly likely. Hence, the results parallel Ag(I) and Cu(I) complexes with an N,S chelating ligand as depicted in Figure 3a.

The observed dynamical behaviour of the Zn(II) complexes is very similar to that of the Ag(I) and Cu(I) complexes. Because binuclear complexes are expected to be more rigid, the Zn(II) complexes are, therefore, most likely also mononuclear units of the $[Zn\{5Me)Im\text{-}SA\text{-}NHCH_2Ph\}_2]^{2+}$ type.

Reverting to the room temperature ^{1}H-NMR data of the Zn(II) complexes again, the large down field shift of the SB-$C_\alpha H_2$ resonance in $[Zn\{(5Me)Im\text{-}SB\text{-}NHCH_2Ph\}_2]^{2+}$ strongly suggest an amide-O–Zn(II) coordination bond. The observation of a $C_\alpha H_2$ resonance in the corresponding SP derived Zn(II) complex, which does not shift markedly, however, may indicate that amide-O coordination is absent in solution. In view of the fact that IR data have established a solid state Zn–O bond with either derivative of **2b** and that all other NMR features of the Zn(II) complexes with the (5Me)Im-SA-$NHCH_2Ph$ as well as the (5Me)Im-SA-Met-Histam ligands (nota bene the pattern change of SA-$C_{\delta/\varepsilon}H_2$) are similar, it is more likely that both have the same structure. CPK molecular model studies do indicate that the Zn–O interaction in $[Zn\{(5Me)Im\text{-}SP\text{-}NHCH_2Ph\}_2]^{2+}$ is probably weaker, as a result of the increased flexibility of the longer chain connecting imidazole-N^3 and amide-O donor atoms, than in $[Zn\{(5Me)Im\text{-}SB\text{-}NHCH_2Ph\}_2\}^{2+}$. In particular in solution, the latter effect may contribute, possibly causing the absence of a substantial SP-$C_\alpha H_2$ shift change in $[Zn\{(5Me)Im\text{-}SP\text{-}NHCH_2Ph\}_2]^{2+}$.

The chelating coordination of a (5Me)Im-SA-$NHCH_2Ph$ ligand via N- and O-atoms, also brings the thioether sulphur in the proximity of the Zn(II) centre. Yet, an additional (weak) Zn-S bond seems rather unlikely because (i) N,S,O coordination implies two neighbouring chelate rings with small bite angles at the Zn(II) centre, which is unfavourable, (ii) the behaviour of all metal complexes is comparable, while a tridentate coordination is expected to be less dynamical than a bidentate one, and (iii) evidence exists that the Zn(II) cations, in addition to the N_2O_2 donor set provided by the ligands, can also bind the solvent, leaving no room for a sulphur interaction. Hence, the results support the hypothetical N,O chelating coordination to Zn(II), as shown in Figure 3b.

STRUCTURE OF THE $[M(n)\{\mathbf{2a}\}]^{n+}(O_3SCF_3^-)_n$ COMPLEXES

Analogous to the donor environment provided by two (5Me)Im-SA-$NHCH_2Ph$ molecules, M:L = 1:1 complexes of (5Me)Im-SA-Met-Histam are expected to possess a more or less tetrahedral coordination geometry, having an N_2S_2 [M = Ag(I) or Cu(I)] or an N_2O_2 [M = Zn(II)] donor set. However, the overall structure of the (5Me)Im-SA-Met-Histam complexes can be predicted less easily. The closely related ligand (5Me)Th-Met-Histam **1a** is shown to have a conformation which is almost maximally stretched out, thus giving rise to oligomeric solution structures of its Ag(I) and Cu(I) complexes [2b]. Therefore, (5Me)Im-SA-Met-Histam most likely has a similar flat structure resulting in comparable oligomeric coordination complexes.

In view of the structures of the $[M(I)\{(5Me)Im\text{-}SA\text{-}NHCH_2Ph\}_2]^+$ complex cations (vide supra), the hypothetical coordination structure for Ag(I) and Cu(I) complexes of (5Me)Im-SA-Met-Histam, therefore comprises a ligand molecule that stretches out over three separate M(I) nuclei (Fig. 4a).

In case of the Zn(II) complexes of (5Me)Im-SA-Met-Histam, it is more difficult to predict a structure. The specific gauche conformation of the "imidazole-amide" fragment of the Met-Histam subunit [2], makes it unlikely that the imidazole-N^3 and amide-O will bind the same Zn(II) centre. For the other subunit (5Me)Im-SA, we propose an N,O chelating coordination in $[Zn\{(5Me)Im\text{-}SA\text{-}NHCH_2Ph\}_2]^{2+}$ but its bonding mode is not necessarily retained when connected to a Met-Histam fragment: e.g. a chelating O–Zn–O coordination could be possible instead. CPK molecular model studies indicate that, in view of the expected tendency of (5Me)Im-SA-Met-Histam to stretch out, at most one donor atom pair can bind in a chelating way. Hence, the most likely Zn(II) complex structure involves either a quadridentate binding ligand (depicted in Figure 4b) or a tridentate one.

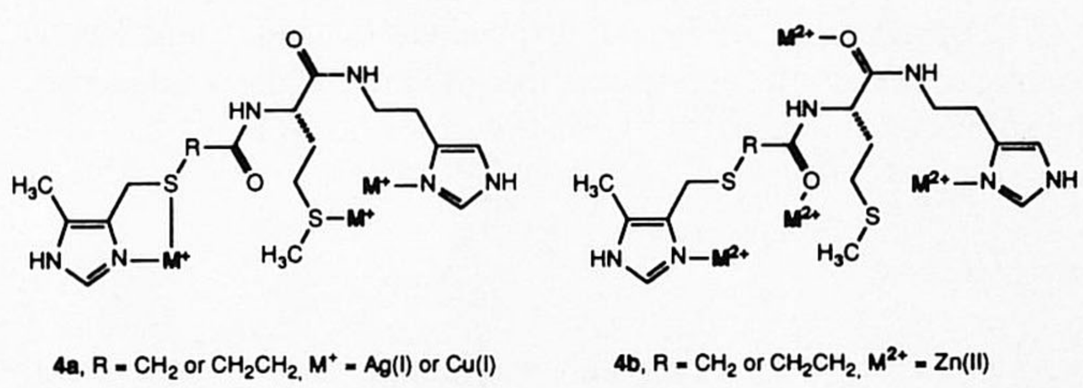


Figure 4. – Proposed binding of (5Me)Im-SA-Met-Histam towards either Ag(I)/Cu(I), **4a**, or Zn(II), **4b**.

The most obvious feature of the present class of complexes, is the fact that the ^{1}H-MNR resonances of the $[Cu\{(5Me)Im\text{-}SA\text{-}Met\text{-}Histam\}]^+$ complex cation are broad over the whole temperature range. Although the determination of the exact Cu(I) coordination geometry is, therefore, severely hampered, it is clear that at least the imidazole rings do coordinate via the N^3-atoms. As pointed out by us [2b] it is rather unlikely that this broadening is to be attributed to the quadrupole nuclear spin moment of Cu(I) [5]. Instead, a relaxation contribution by the paramagnetic Cu(II), ion formed as a result of an intramolecular electron shift equilibrium involving Cu(I)-imidazole and Cu(II)-imidazole$^{\bullet-}$ transitions, seems a more likely explanation. In this respect, it may seem strange that the broadening is less prominent in the $[Cu\{(5Me)Im\text{-}SA\text{-}NHCH_2Ph\}_2]^+$ complexes, in which the Cu(I) ion is coordinated by two imidazole functions, than in complexes which have only one imidazole group per Cu(I) centre [2b, 5]. However, it seems plausible that the effect is cancelled when two imidazole rings occupy (more or less) trans positions relative to the cation. Hence, the drastic enhancement of the broadening observed in the Cu(I) complexes of (5Me)Im-SA-Met-Histam indicates that the metal coordination environment is rather asymmetric in that case.

In the Ag(I) complexes, the imidazole N^3-atoms of both imidazole groups do coordinate, as is evidenced by the considerable downfield shift of the imidazole-H^2 and -H^5 resonances. The shift change of the methionine-$C_\varepsilon H_3$ group, though less obvious, suggests thioether S-atom coordination. The pattern change from an apparent triplet to a multiplet [14] observed for Histam-$C_\alpha H_2$, is attributable to spatial fixation of the "imidazole-amide" fragment. In view of the presence of enough stronger donors, the fixation is not likely caused by an amide-O coordination bond; the Ag–O interaction is probably no more than a dipole-cation attraction. The latter may be reflected in the smaller increase in chemical shift difference of the Histam-$C_\alpha H_2$ spin system in $[Ag\{(5Me)Im\text{-}SA\text{-}Met\text{-}Histam\}]^+$, as compared with **1b**, in which a weak amide-O coordination is found [2]. All other observed trends in the chemical shifts are in agreement with a Ag(I) coordination geometry which is basically a combination of the structures of the separate building blocks.

As in the Cu(I) and Ag(I) complexes, the imidazole-H^2 and -H^5 resonances in the Zn(II) complexes are shifted to low field, indicating coordination of both the imidazole N^3-atoms. The spatial fixation reflected in the pattern change of Histam-$C_\alpha H_2$, is in this case most likely caused by an actual Zn–O bond. The pattern change from a singlet to an AB pattern observed for the SA-$C_{\delta/\varepsilon}H_2$ spin system, may indicate spatial fixation of the (5Me)Im-SA subunit. However, it is unclear whether this fixation is not only identical to but also stronger than in $[Zn\{(5Me)Im\text{-}SA\text{-}NHCH_2Ph\}_2]^{2+}$ or if it represents a different structure.

In summary, although the results obtained for the M:L = 1:1 Ag(I) and Zn(II) complexes of (5Me)Im-SA-Met-Histam are not completely evident, there are no indications that the expected N,N′,S,S′ and N,N′,O,O′ coordination geometries are not formed. In view of the fact that Ag(I) and Cu(I) complexes are virtually always isostructural [25], the latter most likely possess a metal environment with a donor-array similar to its Ag(I) counterpart.

Finally, these Ag(I) and Zn(II) complexes are almost certainly oligomeric species, as can be derived from the ^{1}H-NMR spectra, notably the onset of a signal broadening at relatively high temperature (~ 273 K) culminating in a complete signal collapse at temperatures which are way above the melting point of the solvent [26]. In the case of the $[Ag\{(5Me)Th\text{-}Met\text{-}Histam\}]^+$ complex cation **1b**, we have shown that these phenomena most likely relate to chemical shift anisotropy, caused by a reduction of the tumbling rate at lower temperatures, associated with macromolecular structures like oligomers [2b]. The fact that only one set of ^{1}H resonances is observed at all times, suggests that the present oligomerization of (5Me)Im-SA-Met-Histam does proceed in a stereoregular way.

Conclusions

The 4-imidazolylmethylidenesulfide moiety, which is incorporated in either the N,S,O donor ligand N-[(*n* + 1)–(5-methyl-4-imidazolyl)-*n*-thiaalkanoyl]benzylamine or the chiral N,N′,S,S′,O,O′ donor ligand N-[N-{(*n* + 1)-(5-methyl-4-imidazolyl)-*n*-thiaalkanoyl}-L-methionyl]histamine (*n*-thiaalkanoyl = 3-thiabutanoyl or 4-thiapentanoyl), indeed acts as an N,S chelating function towards Ag(I) and Cu(I) cations.

It is difficult to establish the actual structures of the Ag(I), Cu(I) and Zn(II) complexes with the N,N′,S,S′,O,O′ donor ligand in an M:L = 1:1 stoichiometry, without the help of an X-ray structure determination. The available spectroscopic data, however, suggest that these complexes are oligomeric species in solution. Analogous to the previously reported structure of $(Ag[(5Me)Th\text{-}Met\text{-}Histam]^+)_\infty$, it is proposed that these oligomers are formed as a result of the fact that each ligand stretches out over at least three metal nuclei.

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[15] δ(ppm): 4.8-5.1, singlet of CD_3OH; 3.30. quintet of CD_2HOD.

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[26] Especially when containing a dissolved compound, CD_3OD does not have a clear melting point. Usually, its viscosity only becomes noticeable below ~ 190 K.