Z. anorg. allg. Chem. **517** (1984) 235—240 J. A. Barth, Leipzig

A Potentiometric Study of the Ag^I Complexes of Some Sulphur Containing Amino Acids[*]

J. J. TOMBEUX, J. SCHAUBROECK, C. T. HUYS, H. F. DE BRABANDER, and A. M. GOEMINNE*

Ghent (Belgium), Laboratorium voor Algemene en Anorganische Chemie, Rijksuniversiteit

Abstract. The complex formation of silver(I) with some sulphur-containing amino acids was studied in aqueous solution by simultaneous pH and pM measurements at 25 °C and at an ionic strength of 0.5 M(K)NO_3. In acid medium complex formation occurs only through the thioether group and the carboxylate group is not involved. In alkaline medium both the thioether and the amino group are bound in either the tetrahedral AgL and AgL_2^- chelates or the linear dinuclear Ag_2L_2 species.

Potentiometrische Untersuchungen über Silber(I)-Komplexe einiger schwefelhaltiger Aminosäuren

Inhaltsübersicht. Die Komplexbildung von Silber(I) mit einer Reihe von schwefelhaltigen Aminosäuren wurde durch simultane pH- und pM-Messungen bei 25 °C in 0,5 M(K)NO_3 Lösung untersucht. In saurem Milieu findet die Koordination mit der Thioether-Gruppe statt; die Carboxylat-Gruppe ist nicht beteiligt. In alkalischem Milieu sind die Liganden über S und N dem Ag^1-Ion zugeordnet, und zwar sowohl in den tetraedrischen AgL- und AgL_2^--Chelat-Komplexen als auch in dem linearen dinuclearen Ag_2L_2-Komplex.

Introduction

As the Ag^I ion behaves as a typical soft acceptor [1] the Ag^+-S bond can be expected to be very important in the Ag^I complexes of sulphur-containing amino acids. Such ligands however also contain two other donor groups, i. e. NH_2 and COO^-. It has been shown by PETTIT et al. [2] in a ^1H-n.m.r. study that the carboxylate group was not involved in complex formation and that above pH = 5 these ligands are bound through both the amino and thioether groups either as bidentates in the tetrahedral AgL and AgL_2^- chelates, or are linearly coordinated around the Ag^I ion in the Ag_2L_2 dimer. The behaviour of sulphur containing aminoacid ligands may thus best be compared to that of sulphur containing amines, for which we already could deduce from a thermodynamic study [3—6] an analogous complexation scheme.

The aim of this study is to determine the stabilities of the different species formed between Ag^I and some sulphur-containing amino acids, and to compare the results with those of the corresponding amines [3] and with the findings of the ^1H-n.m.r. results [2].

Experimental

Reagents. The ligands used are listed in Table 1. S-(2-aminoethyl)-mercaptoacetic acid and S-(2-aminoethyl)-3′-mercaptopropionic acid were prepared by dropwise addition of an equivalent amount of ethylene imine and ammonia to a cooled aqueous solution of mercaptoacetic or -propionic acid. The precipitate which formed almost immediately, was recrystallised twice from water-ethanol mixtures and dessicated on P_2O_5. S-ethyl-L(+) cysteine was prepared by addition of an equivalent amount of an alcoholic ethylbromide solution to the fully neutralized L(+) cysteine hydrochloride. The mixture was refluxed until the test with sodium nitroprusside was negative. Precipitation of the product was obtained by acidification to pH = 6, followed by recrystallisation from water. The other amino acids were commercially available. All other reagents were analytical grade. All solutions were made up to an ionic strength of 0.5 with potassium nitrate.

Procedure. Simultaneous pH and pM measurements were performed using two Radiometer potentiometers pHM 64, an Ingold HA 201 glass-electrode, an Orion 94—16A silver electrode, an

Table 1 Ligands

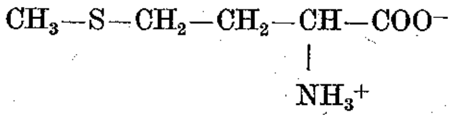
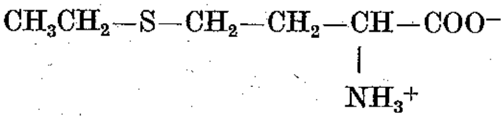
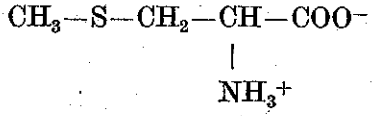
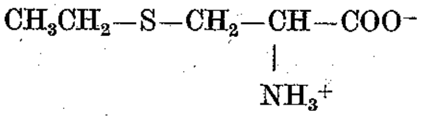
Ligand	Formula	Abbr.
S-(2-aminoethyl)-mercaptoacetate	$H_2N-CH_2-CH_2-S-CH_2-COO^-$	2,2-NSO
S-(2-aminoethyl)-mercaptopropionate	$H_2N-CH_2-CH_2-S-CH_2-CH_2-COO^-$	2,3-NSO
DL-methionine	 $CH_3-S-CH_2-CH_2-\underset{\underset{NH_3^+}{\vert}}{CH}-COO^-$	DL-METH
DL-ethionine	 $CH_3CH_2-S-CH_2-CH_2-\underset{\underset{NH_3^+}{\vert}}{CH}-COO^-$	DL-ETH
S-methyl-cysteine	 $CH_3-S-CH_2-\underset{\underset{NH_3^+}{\vert}}{CH}-COO^-$	SMC
S-ethyl-cysteine	 $CH_3CH_2-S-CH_2-\underset{\underset{NH_3^+}{\vert}}{CH}-COO^-$	SEC

Table 2 Concentration conditions used for 2,3-NSO

Code[a)]	C_H	C_L	C_M	T_{base}	V[b)]	pH-range
	0.1336	0.0636	—	0.9780	55.0	2.2—11.4
	0.0890	0.0420	—	0.9780	50.0	2.3—11.4
F_1 ●	0.0638	0.0560	0.0280	1.0345	50.0	2.1—12.3
F_1 ○	0.0319	0.0280	0.0140	1.0345	50.0	2.4—12.3
F_1 ×	0.0159	0.0140	0.0070	1.0345	50.0	2.6—12.3
F_1 ▼	0.0096	0.0070	0.0035	1.0345	50.0	2.6—12.3
F_2 ×	0.0638	0.0560	0.00028	0.9968	50.0	2.1—12.4
F_2 ○	0.0638	0.0560	0.00014	0.9968	50.0	2.1—12.4
	0.0319	0.0280	0.0420	0.9968	50.0	2.4—7.8

a) Refers to Fig. 1 and 2; b) Initial volume in the titration vessel (cm³)

Ingold 303-NS calomel electrode, and an Ingold 303—95 salt bridge containing 0.5 M KNO_3. All measurements were carried out at 25 °C. The titration procedure was as described before [3]. The concentration conditions used for 2,3-NSO are given as an example in Table 2.

Results and Mathematical Treatment

As could be expected it was found that complex formation gradually increased from acid to alkaline medium. In acid medium the complex formation was studied by the method of LEDEN [7] carried out at several nearly constant pH values. The estimations of the stability constant thus obtained were confirmed by the method of RINGBOM and HARJU [8]. Following that graphical method, preliminary values for the stability constants of the mononuclear monoligand species can be obtained from a function F_1 plotted against pH and those of the mononuclear biligand species from a function F_2:

$$F_1 = pM + \log \frac{(C_M - M)}{(C_L - C_M + M)} + \log \alpha_{L(H)} = \log \beta_{ML} + \log \alpha_{ML(H)}$$

$$F_2 = pM + \log \frac{(C_M - M)}{(C_L - C_M + M)^2} + 2 \log \alpha_{L(H)} = \log \beta_{ML_2} + \log \alpha_{ML_2(H)}$$

where $\alpha_{L(H)}$, $\alpha_{ML(H)}$ and $\alpha_{ML_2(H)}$ are the so-called side reaction coefficients [8].

In Fig. 1 the function F_1 for 2,3-NSO, calculated from titrations with a C_M/C_L ratio of 1/2 (see Table 2) is given as an example and in Fig. 2 the function F_2 calculated from titrations with an excess of ligand is given. In acid medium all points for the various titrations in both Fig. 1 and 2 fit to one curve, indicating that only mononuclear complexes are formed. From these curves estimations for the stability constants of the protonated species could be graphically determined as described elsewhere [8]. In alkaline medium the F_2 values for the different titrations still lie on one curve indicating that AgL_2^- is the only complex formed under these circumstances. The F_1 curves however depend on the total metalion concentration used. It can be shown [8] that in this case polynuclear

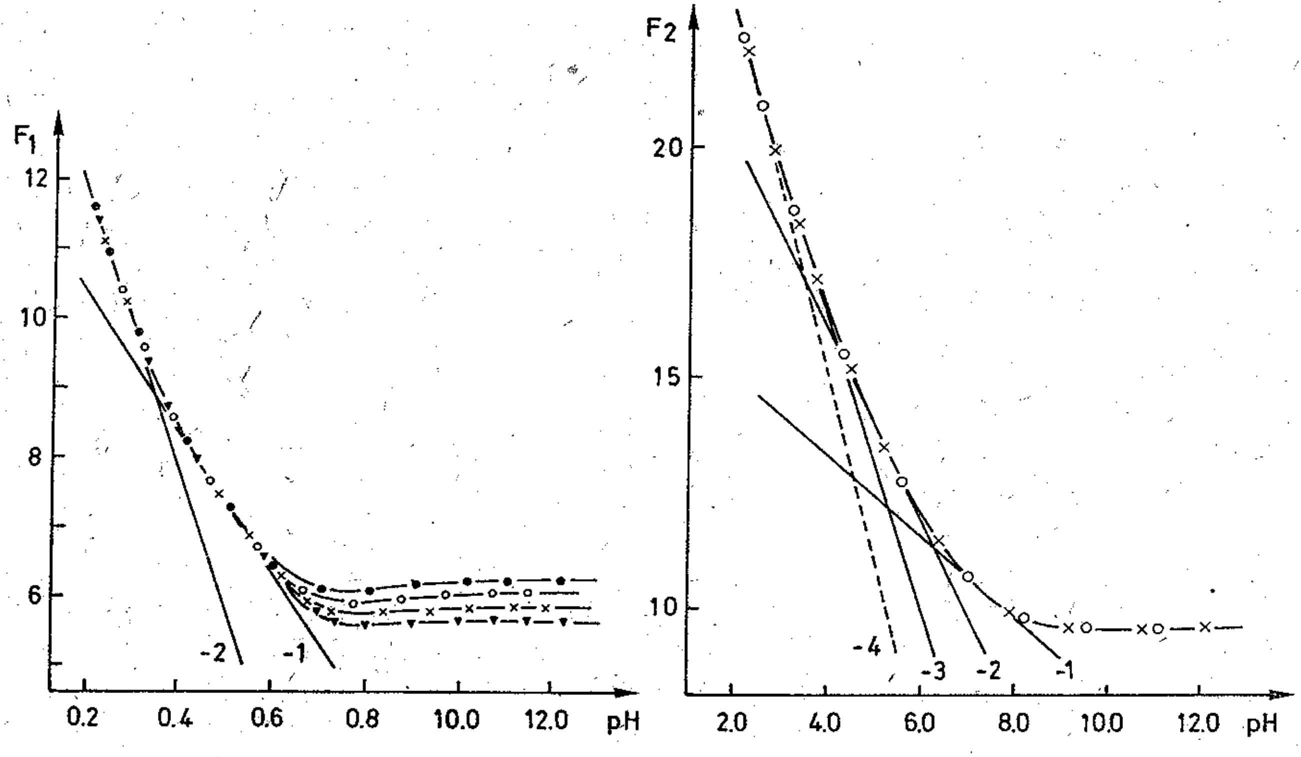


Fig. 1

Fig. 2

Fig. 1 and 2 Ringbom curves of the system Ag^+ and 2,3-NSO (see Table 2) or polymeric complexes are formed. The present behaviour of the F_1-function compares very well with that for the sulphur-containing amines [3] so that also here the Ag_2L_2 complex may be the most probable species.

The ultimate composition was determined and the refinement of the stability constants was performed by a least squares program LSQR [3], a variant of the program LEAST, developped by SABATINI and VACCA [9]. For all other ligands the same procedure was applied and the refined stability constants obtained by the minimization procedure are listed in Table 3. These results may be compared to those of the corresponding amines, given in Table 4.

Table 3 Protonation and stability constants[a]) [b])

Reaction	2,2-NSO	2,3-NSO	SMC	SEC	DL-METH	DL-ETH
$H^+ + L \rightleftarrows HL$	9.534(1)	9.498(1)	8.780(1)	8.73(1)	9.089(1)	9.096(1)
$H^+ + HL \rightleftarrows H_2L^+$	3.181(3)	3.938(3)	1.999(1)	2.05(2)	2.199(3)	2.227(3)
$Ag^+ + H_2L^+ \rightleftarrows Ag(H_2L)^{2+}$	1.95(1)	2.36(2)	2.16(1)	1.57(1)	3.11(2)	3.44(2)
$Ag^+ + HL \rightleftarrows Ag(HL)^+$	2.61(1)	2.78(2)	2.47(1)	2.88(1)	3.37(1)	3.75(1)
$Ag^+ + L^- \rightleftarrows AgL$	5.15(7)	5.1(3)	5.06(4)	5.18(6)	4.8(2)	5.1(1)
$Ag^+ + 2H_2L^+ \rightleftarrows Ag(H_2L)_2^{3+}$	2.75(6)	3.77(3)	3.16(6)	3.4(1)	5.40(2)	5.94(1)
$Ag^+ + H_2L^+ + HL \rightleftarrows Ag(H_2L)(HL)^{2+}$	3.91(3)	4.45(4)	3.91(2)	4.49(2)	5.88(1)	6.49(1)
$Ag^+ + 2HL \rightleftarrows Ag(HL)_2^+$	4.44(1)	4.64(2)	4.00(2)	4.53(1)	5.88(1)	6.37(1)
$Ag^+ + HL + L^- \rightleftarrows Ag(HL)(L)$	7.75(1)	8.17(2)	7.39(2)	8.01(2)	7.38(1)	8.04(1)
$Ag^+ + 2L^- \rightleftarrows AgL_2^-$	9.21(1)	9.61(1)	9.46(1)	9.77(1)	7.88(1)	8.34(1)
$2Ag^+ + 2L^- \rightleftarrows Ag_2L_2$	13.22(5)	13.5(1)	13.06(3)	13.65(3)	13.49(2)	14.09(2)
$2Ag^+ + L^- \rightleftarrows Ag_2L^+$	7.37(2)	7.61(4)	7.08(3)	7.46(2)	7.46(2)	7.93(1)

[a]) 25 °C, 0.5 mole · dm^{-3} $(K)NO_3$; [b]) Value in parenthesis is the standard deviation on the last significant figure.

Table 4 Stability constants of Ag^I with some sulphur containing amines[a])

Reaction	$2\text{-}NS(CH_3)$	$2\text{-}NS(C_2H_5)$	$3\text{-}NS(CH_3)$
$H^+ + L \rightleftarrows HL^+$	9.470(1)	9.441(1)	10.096(1)
$Ag^+ + HL^+ \rightleftarrows AgHL^{2+}$	2.64(1)	2.99(1)	3.33(1)
$Ag^+ + L \rightleftarrows AgL^+$	4.88(6)	5.1(1)	4.8(1)
$Ag^+ + 2HL^+ \rightleftarrows Ag(HL)_2^{3+}$	4.06(2)	4.66(1)	5.60(1)
$Ag^+ + 2L \rightleftarrows AgL_2^+$	9.29(1)	9.66(1)	7.82(1)
$2Ag^+ + 2L \rightleftarrows Ag_2L_2^{2+}$	13.01(4)	13.66(4)	13.69(1)
$2Ag^+ + L \rightleftarrows Ag_2L^{2+}$	6.86(6)	7.42(3)	7.20(2)

[a]) Data from ref. [3], given for comparison.

Discussion

In strong acid medium, where the $Ag(H_2L)^{2+}$ and $Ag(H_2L)_2^{3+}$ complexes are formed, both the amino and carboxylate group are protonated so that complexation only occurs through the sulphur atom. Upon deprotonation of the carboxylic group the complexes $Ag(HL)^+$, $Ag(H_2L)(HL)^{2+}$, and $Ag(HL)_2^+$ are formed.

The stability increases only slightly probably due to a difference in inductive effect between the carboxylic and carboxylate group. The order of magnitude of the stability constants for all these species may be best compared to that of the Ag^I complexes of other thioether ligands [10].

At still higher pH values the complexes AgL_2H, AgL_2^-, Ag_2L_2 and to a less extent AgL and Ag_2L^+ are formed. The stability constants for the latter species are much higher than those for the species in acid medium. That may be an indication for probable chelation through S and N. To confirm the assumptions made above we considered the investigated ligands as thioethers R_1-S-R_2 with S as coordinating centre and R_1 and R_2 as substituents. As the Ag^+-S bond has mainly a σ-bond character [11] the effect of the substituents should be obvious. If chelation occurs, the stability should be markedly higher than could be expected if the amino group e. g. only excerted an inductive effect. In Fig. 3 and 4 we plotted respectively the stability constants of the species AgL′ and AgL_2', where L′ stands for H_2L^+, HL or L^-, versus the sum of the σ^* Taft values of the substituents R_1 and R_2. The σ^* parameters were taken from a compilation by CHARTON [12]. Although the σ^*-parameters are subject to large errors, it may be seen that the AgL′ complexes can be separated into two groups. In the first group, containing the species $Ag(H_2L)^{2+}$ and $Ag(HL)^+$, the amino function

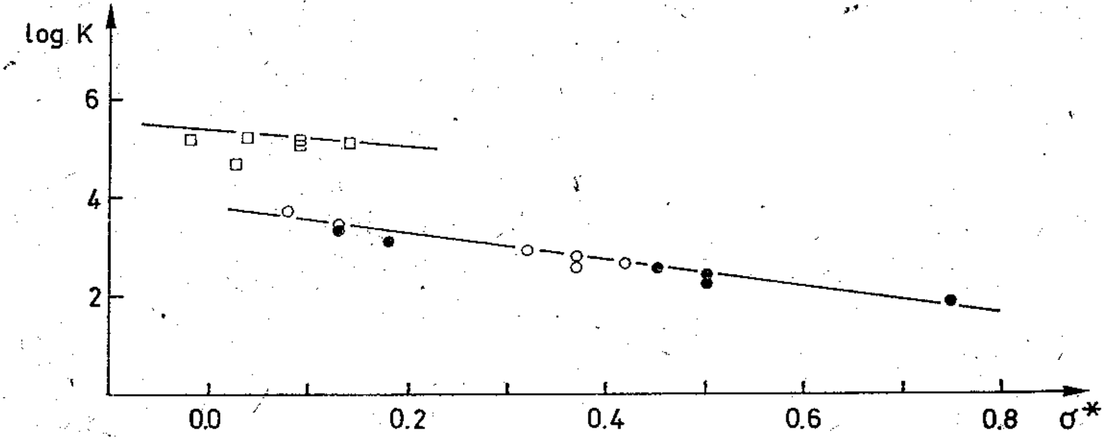


Fig. 3 The relationship between the stability constants of the AgL′ complexes and the Taft-σ^* parameters; $L' = L^-$ (□); HL (○); H_2L^+ (●)

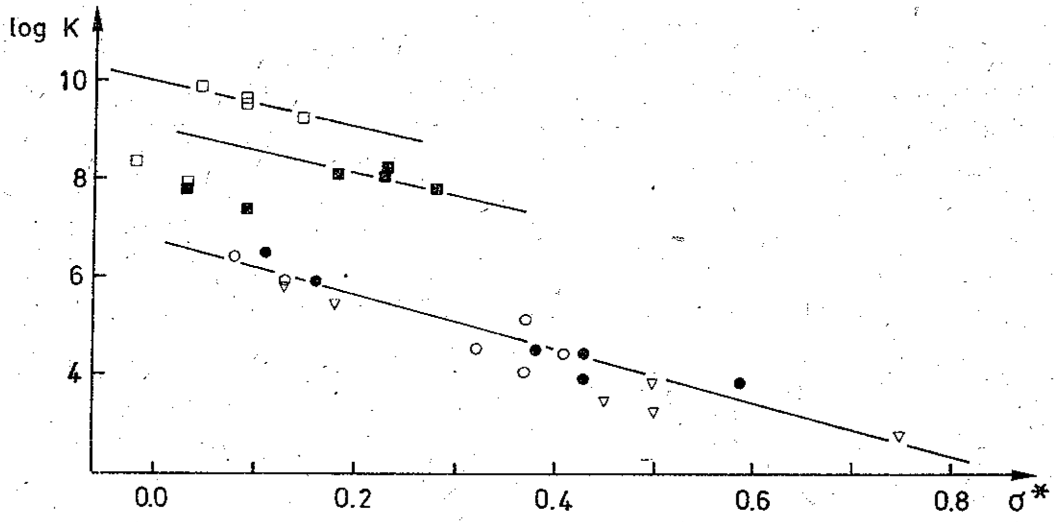


Fig. 4 The relationship between the stability constants of the AgL_2' complexes and the Taft-σ^* parameters; $L' = L^-$ (□); L^- and LH (■); HL (○); H_2L^+ and HL (●); H_2L^+ (▽)

is protonated and the question arises whether the carboxylic group participates in coordination or not. Thus the carboxylate group seems not to interact with the Ag^I ion and the stability decreases with increasing electron withdrawing power of the substituents. This confirms the ^1H-n.m.r. results of Pettit [2]. In the second group the amino function is deprotonated and the stability of the AgL complexes is much larger than could be expected if the amino function only excerted an inductive effect. Chelation through S and N seems therefore to be a possible explanation. The AgL_2^- complexes (see Fig. 2) show the same classification except that an intermediate group is formed for the AgL_2H species where the amino function of one of the coordinated ligands is protonated. Fig. 3 and 4 may be best superimposed on the analogous figures for the sulphur-containing amines, published earlier [3]. Comparing the stability of the AgL_2^- chelates of SMC with DL-METH, of SEC with DL-ETH and of 2-NS(CH_3) with 3-NS(CH_3), a constant difference of about 1.5 log K units is observed. This confirms the higher stability of the five-membered chelate rings versus the six-membered ones.

The structures of the dimeric Ag_2L_2 compound can be explained by dimerization of AgL to a ring compound in which each silver ion is linearly surrounded by a thioether and an amino donor group each originating from a different ligand. The stability of this compound increases from SMC to SEC, from DL-methionine to DL-ethionine and from 2-NS(CH_3) to 2-NS(C_2H_5) with about 0.6 log K units and is also due to a more favourable inductive effect. On the other hand the stability of this dinuclear compound also increases with increasing distance between both charged Ag^I ions: about 0.4 log K units between SMC and DL-METH, SEC and DL-ETH and 0.6 log K units between 2-NS(CH_3) and 3-NS(CH_3). A difference of 0.4 log K units is seen between the analogous dinuclear Ag_2L^+ species and may be explained by the same effect.

The authors wish to thank Prof. G. van der Kelen for helpful discussions and Mr. W. Lippens for technical assistance.

References

[1] Pearson, R. G.: J. Chem. Educ. **45** (1968) 581.
[2] Pettit, L. D.; Siddiqui, K. F.: Inorg. Chim. Acta **55** (1981) 87.
[3] Tombeux, J. J.; Goeminne, A. M.; Eeckhaut, Z.: J. Inorg. Nucl. Chem. **39** (1977) 1655.
[4] Tombeux, J. J.; Goeminne, A. M.; Schaubroeck, J.: Thermochim. Acta. **19** (1977) 327.
[5] Schaubroeck, J.; Goeminne, A. M.: Z. anorg. allg. Chem. **507** (1983) 213.
[6] Schaubroeck, J.; Tombeux, J. J.; Goeminne, A. M.: Thermochim. Acta **677** (1984) 407.
[7] Leden, I.: Sv. Kem. Tidskr. **6** (1946) 129.
[8] Ringbom, A; Harju, L.: Anal. Chim. Acta **59** (1972) 33.
[9] Sabatini, A.; Vacca, A.: J. Chem. Soc., Dalton Trans. **1972**, 1693.
[10] Widmer, M.; Schwarzenbach, G.: Chimia **24** (1970) 447.
[11] Pettit, L.; Sherrington, C.: J. Chem. Soc. **A** (**1968**) 3078.
[12] Charton, M.: J. Org. Chem. **29** (1964) 1222.

Bei der Redaktion eingegangen am 15. Februar 1984.

Anschr. d. Verf.: Dr. A. M. Goeminne, Lab. Algemene en Anorg. Chemie Rijksuniversiteit,
Krijgslaan 281, B-9000 Ghent (Belgium)