

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

COMPLEXES WITH PYRROLE LIGANDS II. THE STABILITY OF THE COMPLEXES OF AG(I) WITH 2-(4-SULFONYL)-PYRRYLMETHYL-METHYL-AMINE

Hans Stünzi^a; Giorgio Anderegg^a

^a Laboratorium für Anorganische Chemie, ETHZ, Zürich, Switzerland

To cite this Article Stünzi, Hans and Anderegg, Giorgio(1978) 'COMPLEXES WITH PYRROLE LIGANDS II. THE STABILITY OF THE COMPLEXES OF AG(I) WITH 2-(4-SULFONYL)-PYRRYLMETHYL-METHYL-AMINE', *Journal of Coordination Chemistry*, 7: 4, 239 – 243

To link to this Article: DOI: 10.1080/00958977808079917

URL: <http://dx.doi.org/10.1080/00958977808079917>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

COMPLEXES WITH PYRROLE LIGANDS II. THE STABILITY OF THE COMPLEXES OF AG(I) WITH 2-(4-SULFONYL)-PYRRYLMETHYL-METHYL-AMINE

HANS STÜNZI and GIORGIO ANDEREGG

Laboratorium für Anorganische Chemie, ETHZ, Universitätstrasse 6, CH-8092 Zürich, Switzerland

(Received July 19, 1977)

The silver(I) complexes of 2-(4-sulfonyl)-pyrrylmethyl-methyl-amine (PSMA) in aqueous solution are investigated by means of alkalimetric titrations. The deprotonated pyrrole group stabilizes the Ag^+ complex to an extent similar to that of a 2-pyridyl-methyl or 2'-aminoethyl group with equal basicity.

INTRODUCTION

We have investigated recently¹ by use of some N-substituted 2-(4-sulfonyl)-pyrrylmethyl derivatives of methylamine, glycine, ethylenediamine and iminodiacetic acid the coordinating tendency of pyrrole nitrogen in aqueous solution for Cu^{2+} and Ni^{2+} . In this paper we describe similar investigations on the equilibria between Ag^+ and 2-(4-sulfonyl)-pyrrylmethyl-methyl-amine. This compound has two nitrogen atoms separated by two carbon atoms and therefore can act as a bidentate ligand. In consideration of the special coordination of the cation Ag^+ not only mononuclear complexes are expected: indeed the analogous bidentate N-ligands ethylene-diamine and [(2-pyridyl)methyl]-amine give also bimetallic complexes.²⁻⁴

EXPERIMENTAL

Reagents

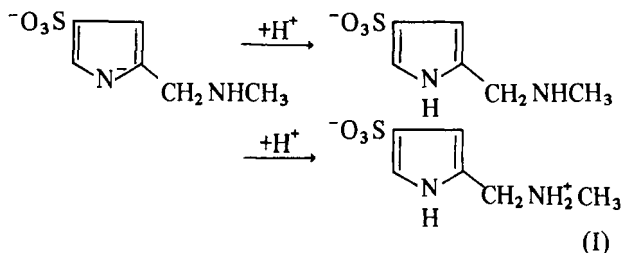
Preparation of the ligand. The synthesis of 2-methylaminomethyl-pyrrole-(4)-sulfonic acid (H_2L) was already described by us.¹

Other reagents. Silver nitrate, potassium nitrate and potassium hydroxyde (Merck, p.a.) are found enough pure and are used without further purification.

Determination of the stability constants. See^{1, 5}. Potassium nitrate was used as an ionic medium in order to keep constant the ionic strength at $I = 1\text{M}$. pH measurements are done in the concentration scale ($\text{pH} = -\log[\text{H}^+]$).

RESULTS

Protonation equilibria of the ligand. As already reported¹ the protonation constants of the ligand are: $\log K_{1,\text{H}} = \log([\text{HL}^-]/([\text{H}^+][\text{L}^{2-}])) = 15.4$ and $\log K_{2,\text{H}} = \log([\text{H}_2\text{L}]/([\text{H}^+][\text{HL}^-])) = 9.58$ at 25°C and $I = 1(\text{KNO}_3)$. They correspond to the protonation of the pyrrolate and the amine nitrogen atom respectively:



Complex formation. The results of alkalimetric titrations of solutions of silver nitrate and protonated ligand in concentration ratios from 1:1 to 1:2 and total ligand concentrations varying from 0.001 to 0.02 M are given in Table I. Preliminary calculations have been done with the program KONST,⁶ in which only complexes of the type ML_n are considered, by use of the relation (1). However, the experimental values of the degree of complex

$$\bar{n} + \sum_{n=0}^{n=N} (\bar{n} - n) \beta_n [\text{L}]^n = 0 \quad (1)$$

formation \bar{n} and of the free ligand concentration $[\text{L}]$ inserted in that relation give in the whole range

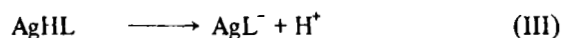
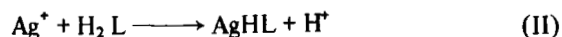
TABLE I

Experimental data (ml x M KOH, pH, 1000 (ml_{calc} - ml_{exp}) in solutions at I = 1 (KNO₃), ml_{exp}: volume of strong base added to the solution of the components containing an excess of strong acid [H]_t; ml_{calc}: calculated volume of strong base using the "best" set of equilibrium constants.

A. [M] _t = 0.00996 M; [L] _t = 0.01001 M; total volume 50.2 ml; x = 0.5; [H] _t = 0.01967 M
2.150, 8.104, -3; 2.200, 8.220, -2; 2.250, 8.315, -3; 2.300, 8.400, -3; 2.350, 8.474, -4; 2.400, 8.544, -3; 2.450, 8.607, -3; 2.500, 8.668, -1; 2.550, 8.724, -1; 2.600, 8.778, 0; 2.650, 8.828, -1; 2.700, 8.878, 0; 2.750, 8.924, -2; 2.800, 8.969, -2; 2.850, 9.015, -2; 2.900, 9.059, -3; 2.950, 9.101, -1; 3.000, 9.145, -1; 3.050, 9.187, -8; 3.100, 9.231, -9; 3.150, 9.275, -11; 3.200, 9.321, -11; 3.250, 9.366, -12; 3.300, 9.415, -12; 3.350, 9.464, -13; 3.400, 9.517, -12; 3.450, 9.571, -13; 3.500, 9.63, -12; 3.550, 9.691, -12; 3.600, 9.759, -12; 3.650, 9.833, -10; 3.700, 9.914, -10; 3.750, 10.007, -8; 3.800, 10.114, -7.
B. [M] _t = 0.02 M; [L] _t = 0.0203 M; total volume 50 ml; x = 0.5; [H] _t = 0.01987 M
2.150, 7.519, +1; 2.250, 7.713, -1; 2.350, 7.853, -1; 2.450, 7.962, -3; 2.550, 8.055, -3; 2.650, 8.138, -2; 2.750, 8.214, 0; 2.850, 8.281, 0; 2.950, 8.346, +2; 3.050, 8.409, +6; 3.150, 8.465, +6; 3.250, 8.522, +9; 3.350, 8.567, +11; 3.550, 8.677, +10; 3.650, 8.725, +8; 3.750, 8.771, +3; 3.850, 8.820, +5; 3.950, 8.866, 0; 4.050, 8.913, -2; 4.150, 8.962, -1; 4.250, 9.011, -1; 4.350, 9.059, -6; 4.450, 9.110, -5; 4.550, 9.162, -3; 4.650, 9.216, -2; 4.750, 9.273, +2; 4.850, 9.331, +2; 4.950, 9.395, +9; 5.050, 9.459, +10; 5.150, 9.532, +17; 5.250, 9.609, +21; 5.350, 9.694, +26; 5.450, 9.791, +32; 5.550, 9.900, +35; 5.650, 10.029, +38; 5.750, 10.185, +39.
C. [M] _t = 0.0049 M; [L] _t = 0.005 M; total volume 50 ml; x = 0.5; [H] _t = 0.01975 M
2.050, 8.286, 0; 2.240, 8.932, +1; 2.430, 9.292, +2; 2.620, 9.614, +1; 2.810, 10.038, +1; 2.900, 10.330, +1.
D. [M] _t = 0.002 M; [L] _t = 0.00202 M; total volume 50 ml; x = 0.1; [H] _t = 0.00398 M
2.200, 8.687, 0; 2.300, 8.885, -1; 2.400, 9.039, -2; 2.500, 9.169, -2; 2.600, 9.279, -3; 2.700, 9.377, -4; 2.800, 9.466, -3; 2.900, 9.547, -5; 3.000, 9.627, -5; 3.100, 9.705, -5; 3.200, 9.782, -5; 3.300, 9.862, -4; 3.400, 9.944, -4; 3.500, 10.029, -3; 3.600, 10.119, -3; 3.700, 10.212, -2; 3.800, 10.306, -1.
E. [M] _t = 0.005 M; [L] _t = 0.01005 M; total volume 50 ml; x = 0.5; [H] _t = 0.01970 M
2.150, 8.317, 0; 2.200, 8.435, +1; 2.250, 8.535, 0; 2.300, 8.623, 0; 2.350, 8.706, +1; 2.400, 8.782, +1; 2.450, 8.854, +1; 2.500, 8.925, +3; 2.550, 8.991, +2; 2.600, 9.059, +4; 2.650, 9.123, +4; 2.700, 9.189, +5; 2.750, 9.253, +5; 2.800, 9.320, +6; 2.850, 9.385, +5; 2.900, 9.456, +6; 2.950, 9.530, +8; 3.000, 9.606, +9; 3.150, 9.684, +8; 3.100, 9.770, +9; 3.150, 9.863, +10; 3.200, 9.963, +11; 3.250, 10.072, +12; 3.300, 10.190, +12; 3.350, 10.317, +12; 3.400, 10.457, +12.
F. [M] _t = 0.002 M; [L] _t = 0.00303 M; total volume 50 ml; x = 0.1; [H] _t = 0.00398 M
2.300, 8.680, +7; 2.400, 8.817, +6; 2.500, 8.932, +5; 2.600, 9.033, +6; 2.700, 9.123, +5; 2.800, 9.205, +5; 2.900, 9.280, +4; 3.000, 9.353, +6; 3.100, 9.421, +6; 3.200, 9.485, +5; 3.300, 9.551, +8; 3.400, 9.612, +5; 3.500, 9.676, +8; 3.600, 9.740, +8; 3.700, 9.806, +9; 3.800, 9.874, +10; 3.900, 9.946, +12; 4.000, 10.020, +11; 4.100, 10.098, +12; 4.200, 10.180, +10; 4.300, 10.264, +7.
G. [M] _t = 0.002 M; [L] _t = 0.00404 M; total volume 50 ml; x = 0.1; [H] _t = 0.00398 M
2.300, 8.530, +5; 2.400, 8.662, +5; 2.500, 8.770, +4; 2.600, 8.863, +3; 2.700, 8.946, +2; 2.800, 9.022, +1; 2.900, 9.093, 0; 3.000, 9.160, +1; 3.100, 9.223, -1; 3.200, 9.284, -1; 3.300, 9.343, 0; 3.400, 9.400, +1; 3.500, 9.456, 0; 3.600, 9.512, +1; 3.700, 9.568, +2; 3.800, 9.623, +3; 3.900, 9.679, +2; 4.000, 9.738, +4; 4.100, 9.796, +1; 4.200, 9.858, +3; 4.300, 9.923, +3; 4.400, 9.992, +5; 4.500, 10.062, +4; 4.600, 10.137, +4; 4.700, 10.215, +3.

inconsistent values for the overall formation constants β_1 and β_2 . Only from the experimental points at lower pH values, under the assumption that HL⁻ acts as ligand, it was possible to obtain approximative values for the formation of AgHL and Ag(HL)₂⁻.

From an examination of the titration curves (Fig. 1), it appears that in equimolar solutions of the reagents two mole protons per mole ligand are liberated. This is due probably to the overlap of



reactions (II) and (III). On the other hand, for solutions with a ratio between the total concentrations of Ag⁺ and ligand of 1:2 the number of mole protons liberated per mole ligand is 1.5, in agreement with the reactions (II), (IV) and (V), where for the

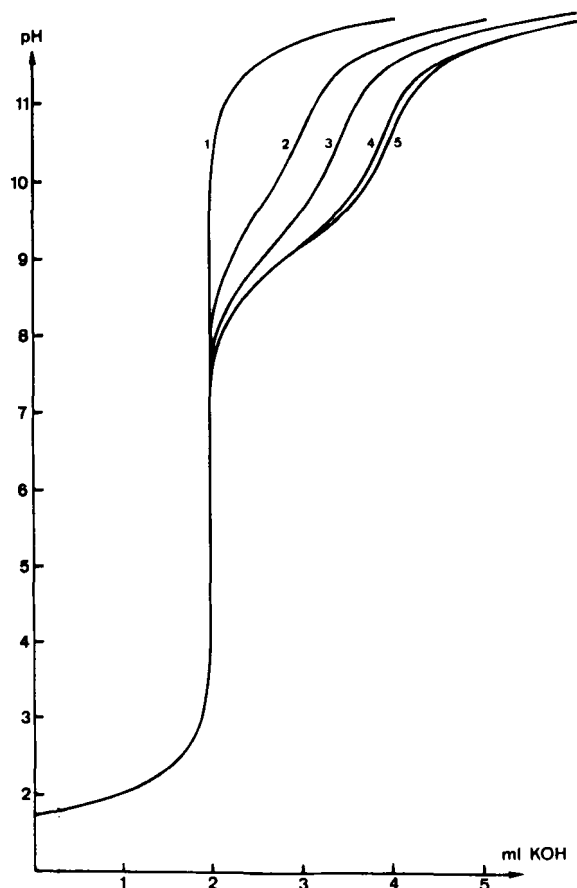


FIGURE 1 Titration curves of 0.01005 M ligand solutions (50 ml) in presence of AgNO_3 and 0.02 M HNO_3 with 0.5 M KOH at 25° and $I = 1(\text{KNO}_3)$.
2: $[\text{Ag}]_t = 0$; 3: 0.0050 M; 4: 0.0090 M; 5: 0.0100 M.
Curve 1: titration curve of 0.02 M HNO_3 .

last reaction the alternative (V') can also be considered. From the literature values⁷ for the hydrolysis



of Ag^+ it follows that only small amounts of AgOH and $\text{Ag}(\text{OH})_2^-$ can be present in the investigated solutions. The definitive calculations with the "best values for the constants" give for the sum of the concentrations of these hydrolytic products values lower than 1% of the total concentration of the metal ion. From the other reactions given above, the equilibria could be explained with the existence of mononuclear species only. Because of the simultaneous

presence of protonated and non-protonated complex ions relation (1) is no more valid. A program (KVARI) is then used, in which species of type $\text{M}_q\text{H}_p\text{L}_n$ can be assumed, with overall constants of the type $\beta_{q,p,n} = [\text{M}_q\text{H}_p\text{L}_n] / [\text{M}]^q [\text{H}]^p [\text{L}]^n$. The sum S of the square of the difference between the experimental and the calculated value of the concentration of strong acid present divided by the total concentration of the ligand (error square sum) is minimized by variation of the values of

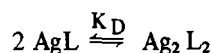
$$S = \sum ([H]_{t,\text{exp}} - [H]_{t,\text{calc}})^2 / [L]_t^2$$

the constants involved in the calculation of $[H]_{t,\text{calc}}$. The standard deviation σ of $[H]_{t,\text{exp}} / [L]_t (= S / (I-i))$; I = total number of experimental points and i = number of constants varied) is also obtained.

With assumption of mononuclear complex ions only (AgHL , $\text{Ag}(\text{HL})_2^-$ and AgL^-) the obtained standard deviation σ is 0.097, i.e. much higher than expected. After introduction of a dimer $\text{Ag}_2\text{L}_2^{2-}$ by variation of all involved constants a new minimum of S is found. A very remarkable decrease of the standard deviation σ is observed, whereas the amount of the species AgL^- becomes negligible and $\beta_{1,0,1}$ can be set equal to zero. As can be seen from Table II by separate addition of the constants for AgHL_2^{2-} , $\text{Ag}_3\text{HL}_3^{2-}$ and $\text{Ag}_3\text{L}_3^{3-}$ lower values of σ are respectively found. Tests for the presence of other species: Ag_2L , $\text{AgL}(\text{OH})^{2-}$, $\text{Ag}_4\text{L}_4^{4-}$, $\text{Ag}_4\text{HL}_4^{3-}$ and $\text{Ag}_2\text{HL}_3^{3-}$ do not improve the results. The composition and the stability constants of the complexes finally accepted are summarized together with the uncertainties of each constant in the last line of Table II. The final value of σ is of the expected magnitude. Further reduction of σ is generally possible, with assumption that each separate titration involves certain systematic errors. This type of refinement was not accomplished, because it is questionable from a statistical point of view.

In comparison with the other bidentate N ligands, ethylenediamine (EN) and (2-pyridyl)methyl-amine (PMA), the pyrrol derivative (PSMA) shows the following peculiarities:

a) The 1:1 complex is not present. An inspection of the results makes evident that the constant for the dimerisation:



is very different for the complexes of the two mentioned amines ($10^{2.27}(\text{EN})^3$ and $10^{5.1}(\text{PMA})^4$). The value of K_D seems to depend strongly on the steric

TABLE II
Stability constants^a calculated under various assumptions (T = 25 ± 0.1°C, I = 1 (KNO₃))

	log β _{1,1,1}	log β _{1,2,2}	log β _{2,1,2}	log β _{2,0,2}	log β _{3,1,3}	log β _{3,0,3}	σ
Titrations ^b A,B,C	18.10(10)	36.40		20.50(20)			0.031
	17.92(10)	36.37	13.8	20.40(10)			0.020
	18.00	36.36		20.34(15)		31.30(50)	0.020
	18.00	36.36		20.27(10)	25.4	36.40(10)	0.015
	17.95	36.36	13.7(5)	20.14	25.4(4)	31.7	0.013
	18.00(10)	36.36	13.7	20.24(8)	25.4	31.55	0.0123
	18.00	36.36	13.7	20.22(10)	25.4	31.60(15)	0.0120
Titrations ^b D,E,F,G	18.1	36.40(10)		20.30(5)			0.008
	18.00	36.42(5)		20.12(5)	25.4	31.55	0.0038
	18.00	36.36(4)	13.7	20.10(4)	25.4	31.55	0.0028
	18.00	36.37	13.7	20.10(3)	25.4	31.53(8)	0.0028
Titrations ^b A,B,C,D,E,F,G	18.00	36.37	13.7	20.08(6)	25.4	31.68(10)	0.0060
	18.00	36.37	13.7(3)	20.08	25.4(2)	31.68	0.0060
	18.00(5)	36.36(6)	13.7	20.08	25.4	31.68	0.0060
	18.00(6)	36.36(4)	13.7(3)	20.09(6)	25.4(2)	31.68(10)	0.0060

^aIn parentheses three times the standard deviation of the last digits. log β_{0,-1,0} = 13.77 and log β_{1,-1,0} = -11.4.

^bSee Table I.

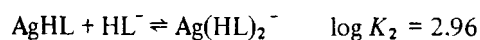
requirements of the ligand, which can only form strained 1:1 complexes with silver(I) by coordination of both nitrogen atoms. A small increase of the value of K_D with respect to the pyridine derivative leads to a system in which only polynuclear species are present. This is probably what happens with the 1:1 PSMA complexes, in which presumably only one nitrogen atom can be coordinated.

b) The species AgL₂ is not formed in the same way as for the ethylenediamine complexes.

c) The complexes Ag₂L (β_{2,0,1} < 10^{9.4}) and AgL(OH) (β_{1,-1,1} < 10^{-3.8}) are not present. However, the concentration of the complex Ag₂L represents in the other systems (EN and PMA) only 1–2% of the total amount of silver ions! Further AgL(OH) is possibly destabilized, because in contrast to the analogous complex with ethylenediamine the 1:1 complex AgL is unstable.

DISCUSSION

Complex formation takes place firstly with the protonated ligand HL⁺ giving AgHL and Ag(HL)₂⁺. Stepwise stability constants of these complexes are calculated from the values of Table II:



The second stability constant K₂ is larger than the first K₁, as found for monoamines (for NH₃: log K₁ = 3.2 and log K₂ = 3.83⁸). For monodentate nitrogen ligands a linear relationship (2) between log β₂ = log(K₁K₂) and the logarithm of their protonation constants K_{1,H} was established.⁹ Taking 3-cyanopyridine, aniline, pyridine and ammonia,⁸⁻¹¹ relationships (3) for the 1:1 complexes was obtained. The calculated

$$\log \beta_2 = 0.77 \log K_{1,H} \quad (2)$$

$$\log K_1 = 0.44 + 0.31 \log K_{1,H} \quad (3)$$

values for the investigated ligand with log K_{1,H} = 9.58 are log β₂ = 7.38 and log K₁ = 3.4, i.e. much higher than the experimental values given above, because of the steric hindrance by the methyl group as also found for instance for methylamine¹¹ (log K₁ calculated: 3.75, found: 3.15 and log β₂: calc. 8.25 and found 6.78). It appears therefore, that in these species: AgHL and Ag(HL)₂⁺ the coordination takes place only through the amino nitrogen atom. A further deprotonation seems only possible for AgHL with formation of polynuclear species in which the pyrrolate ion is coordinated. Not only ring structures (Ag_qL_q^{q-}) but also polymeric linear species (Ag_qHL_q^{(q-1)-}) are formed.

For a further discussion we can compare the values of β_{2,0,2} for the three bidentate nitrogen ligands, EN,

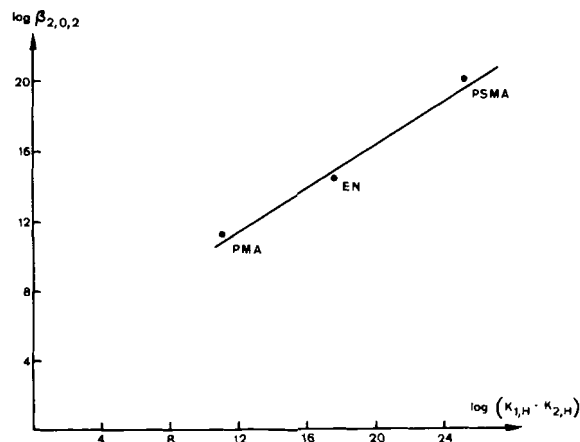


FIGURE 2 Correlation between the stability constants $\beta_{2,0,2}$ and the product of the protonation constants of the ligands.

PMA and PSMA and try to obtain a correlation with the product of the two protonation constants $K_{1,H}$ and $K_{2,H}$ which refer to the two nitrogen atoms involved in the coordination. In this comparison we ignore the differences in the values of $\beta_{2,0,2}$ for the different media used as well as those due to steric strains. For the three 12-membered rings these differences are expected to be small in magnitude. As can be seen in the plot of Figure 2, the three points

are approximately on a straight line. Under the given assumptions the pyrrolate nitrogen atom behaves in the coordination with Ag^+ in a similar way as another nitrogen donor. This conclusion is identical with that formulated by us from the investigation of pyrrole derivatives with Cu^{2+} and Ni^{2+} . This should also be true for the corresponding monodentate ligands: we therefore can apply equations (2) and (3) to obtain the estimated constants for the formation of silver pyrrolate complexes with $\log K_{1,H} = 15.4$. One obtains $\log K_1 = 5.2$ and $\log \beta_2 = 11.2$.

REFERENCES

1. Part I. H. Stünzi and G. Anderegg, *Helv. Chim. Acta*, **59**, 1621 (1976).
2. G. Schwarzenbach, H. Ackermann, B. Maissen and G. Anderegg, *Helv. Chim. Acta*, **35**, 2337 (1952).
3. H. Ohtaki and Y. Ito, *J. Coord. Chem.*, **3**, 131 (1973).
4. A. M. Gouminne and Z. Eeckhaut, *J. Inorg. Nucl. Chem.*, **36**, 357 (1974).
5. H. Stünzi and G. Anderegg, *Helv. Chim. Acta*, **56**, 1698 (1973).
6. G. Anderegg, *Helv. Chim. Acta*, **44**, 1673 (1961).
7. G. Biedermann and L. G. Sillen, *Acta Chem. Scand.*, **14**, 717 (1960).
8. J. Bjerrum, *Metal ammine formation in aqueous solution*, Thesis, 1941, P. Haase and Son, Copenhagen.
9. F. Marsicano and R. D. Hancock, Report No. 1764, National Institute for Metallurgy, Johannesburg 1975.
10. R. Näsänen, *Acta Chem. Scand.*, **1**, 763 (1947).
11. J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).