



Silver(I) and Silver(II) Complexes with Some Tetraazamacrocyclic Ligands in Aqueous Solutions

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Abstract

The reactions of silver(I) with *isocyclam*, *scorpiand*, *trans*-Me₂[14]anN₄, *cis*-Me₆[14]anN₄, (*N*-Me)Me₂py[14]anN₄ and py[12]anN₄ were investigated. The stability constant of the Ag(I) complex with py[12]anN₄ was determined. The aqueous solutions of the silver(II) complexes with the 14-membered ligands were obtained, and characterized by means of UV-VIS and CVA measurements. The Ag²⁺ ion does not form a five-coordinate complex with *scorpiand*. The formal potentials of the Ag(II)/Ag(I) system in the presence of *scorpiand*, *trans*-Me₂[14]anN₄, *cis*-Me₆[14]anN₄ and (*N*-Me)Me₂py[14]anN₄ were determined. The mechanism is also proposed for the electroreduction of the silver(II) complexes with these compounds on a platinum electrode in aqueous solution.

Introduction

Polyazamacrocyclic ligands can stabilize both unusually high and unusually low oxidation states of transition metal ions [1–5]. In particular, tetraazamacrocyclic ligands possessing a suitable size of *bonding cavity* [6] and *hard* nitrogen donor atoms, can form stable complexes with the Ag²⁺ cation in aqueous solution. These compounds are the product of the disproportionation of the Ag(I) complexes with cyclic tetraamines [6–15]. It was found that there are two factors that affect this process [16]: (i) the size of the *bonding cavity* of the ligand and (ii) the properties of the solvent.

Water, as compared to other solvents, for example: dimethylsulfoxide or acetonitrile, is a very good medium for investigating Ag²⁺ ion stabilization. There is the hard oxygen atom in the water molecule, which can better solvate the Ag²⁺ cation (*hard* Pearson's acid) than the Ag⁺ cation (soft Pearson's acid). This causes a reduction of the standard potential of the Ag(II)/Ag(I) system (i.e., Ag²⁺ stabilization) and an increase of the standard potential of the Ag(I)/Ag(0) system.

The ligands: *isocyclam*, *scorpiand*, *trans*-Me₂[14]anN₄, *cis*-Me₆[14]anN₄, and (*N*-Me)Me₂py[14]anN₄ are derivatives of *cyclam* – the most popular tetraazamacrocyclic ligand. Py[12]anN₄ is a derivative of cyclen – another popular tetraazamacrocyclic ligand with a pyridine moiety in the macrocyclic ring. The structures of these cyclic polyamines as well as the names used in this article, are presented in Scheme 1.

The aim of our study was: (i) characterisation of the silver complexes obtained in the presence of *isocyclam*, *scorpiand*, *trans*-Me₂[14]anN₄, *cis*-Me₆[14]anN₄ and (*N*-Me)Me₂py[14]anN₄ in aqueous solution, (ii) investigation of the thermodynamics of the stabilization of silver(II) by these tetraazamacrocyclic ligands, (iii) determination of the mechanism of the electroreduction of the silver(II) complexes on a platinum electrode in aqueous solutions and (iv) to test, if the Ag²⁺ ion, similar to the Ni²⁺ ion, can form a five-coordinated complex with *scorpiand*.

Experimental

The ligands

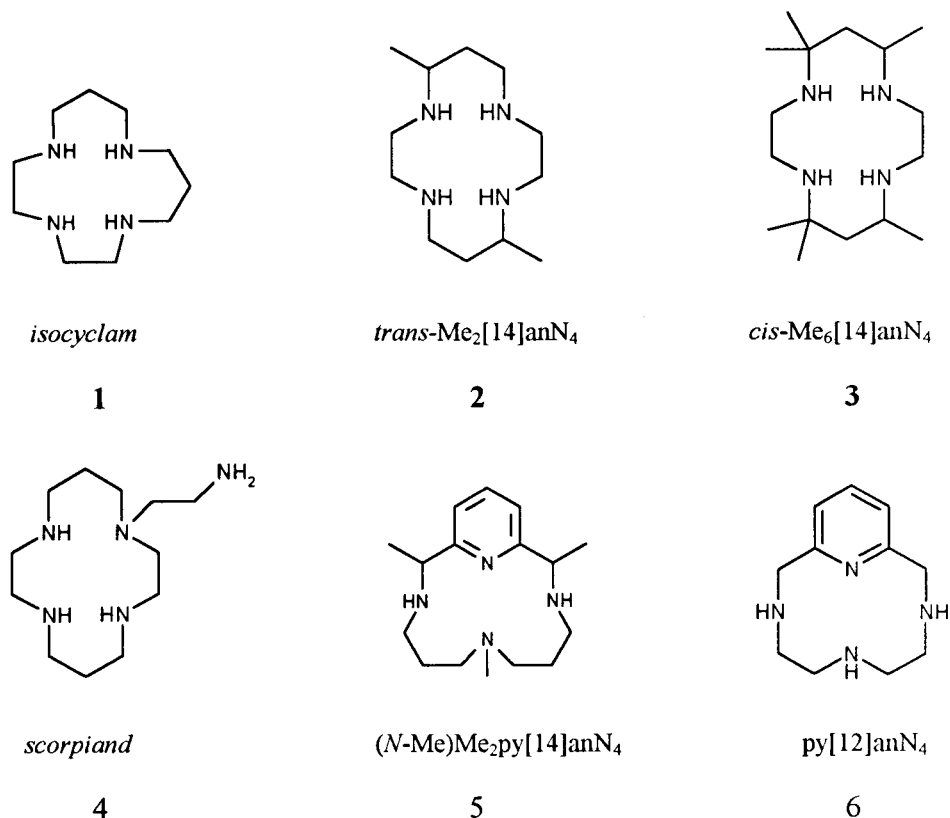
Isocyclam and *scorpiand* were synthesized according to the procedure described in [17] and [18], respectively. Both compounds were analysed by ¹H and ¹³C NMR spectroscopy. The following ligands: py[12]anN₄, *trans*-Me₂[14]anN₄, *cis*-Me₆[14]anN₄ and (*N*-Me)Me₂py[14]anN₄ were synthesized by Prof. Luigi Fabbri's group from the University of Pavia, Italy. The purity of all the ligands was checked by potentiometric titration of their protonation form H₄L⁴⁺ with standard KOH solution (CO₂-free).

Synthesis of the silver(II) complexes

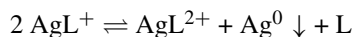
The silver(II) complexes were obtained by the following two methods:

(a) Disproportionation of silver(I) complexes according to the following equation:

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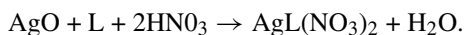
Scheme 1. The structure and the names of the ligands under investigation.



AgNO₃ solution was added to the ligand solution ($c_L = 10^{-3} - 10^{-2} \text{ mol dm}^{-3}$) in a 2:1 molar ratio of Ag²⁺:L. The solutions were intensively stirred for *ca.* 6 hours and protected from light, in order to prevent decomposition of the silver(II) complexes. Then, the solutions were filtered in order to remove the precipitated metallic silver and concentrated on a vacuum evaporator. The silver(II) complexes were obtained as a brown oil with 78–85% yield.

(b) Reaction of the ligand with AgO:

The process occurred according to the following equation:



The silver(II) oxide was synthesized and its purity was checked according to the procedure described in [19]. The stoichiometric amount of AgO was added to the cooled (−10 °C) ligand solution ($c_L \approx 10^{-3} \text{ mol dm}^{-3}$) and the HNO₃ solution was then added dropwise to complete dissolution of the silver(II) oxide. The solution was stirred for 24 hours and protected from light in order to prevent decomposition of the silver(II) complex and then concentrated on the vacuum evaporator. Similar to method (a), the silver(II) complexes were obtained as a brown oil with 68–72% yield.

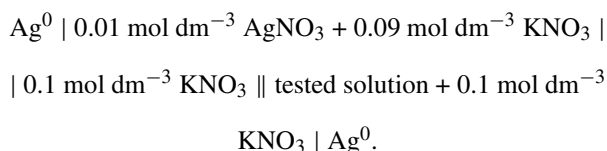
In both cases the silver(II) complexes were obtained as a oil. Thus, determination of the melting point and the elemental analysis of those compounds was not possible. The

presence of Ag²⁺ cation in these complexes was confirmed by UV-VIS measurements (see below).

In the presence of py[12]anN₄ disproportionation of the Ag(py[12]anN₄)⁺ complex did not occur. Moreover, in the reaction of py[12]anN₄ with AgO, the Ag(py[12]anN₄)²⁺ complex was also not formed. In both cases colourless and stable solutions of the Ag(I) complex with this ligand were obtained.

Potentiometric measurements

Potentiometric measurements were used to determine the value of the stability constant of the Ag(I) complex with py[12]anN₄. In this method, the solution of the ligand ($c_L = 5 \times 10^{-4} - 2 \times 10^{-3} \text{ mol dm}^{-3}$) was titrated with standard 0.01 mol dm⁻³ AgNO₃ solution (POCh Gliwice, Poland). The concentration of the free Ag⁺ ions was determined by EMF measurements in the following system:



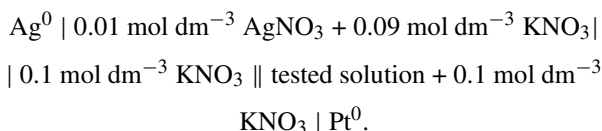
UV-VIS and IR measurements

All UV-VIS measurements were done on a PU 8630 UV/VIS/NIR spectrometer (Philips) in a quartz cuvette with an optical path length of 0.995 cm. The pH values of the

$\text{Ag}(\text{scorpiand})^{2+}$ solutions were changed by addition of the appropriate amount of HNO_3 and were controlled by means of a ESAP-301 (Eurosensor) electrode and a digital pH-meter N-5172 (TelEko). IR measurements were done on a Specord M80 spectrometer (Carl Zeiss Jena) in solid KBr (Aldrich).

The voltammetric and amperostatic coulometry measurements

The voltammetric measurements were made in the three-electrode system:



where platinum wire was the working electrode, the silver electrode was the reference electrode and platinum gauze was the counter electrode. In this study all the potential values refer to the potential of the silver reference electrode, i.e., $\text{Ag}^0 \mid 0.01 \text{ mol dm}^{-3} \text{ AgNO}_3 + 0.09 \text{ mol dm}^{-3} \text{ KNO}_3$. The potentiostat PGSTAT10 from AUTOLAB (Eco Chemie BV) was the generator of the staircase polarization signal of the working electrode. The value of the α parameter was set to 0.707 [20, 21]. A PC computer OptiPlex GL575 (Dell) with GPES v. 4.5 (Eco Chemie BV) software was used to record and analyze the voltammetric curves.

The amperostatic conditions during the coulometry measurements were adjusted by a PX unit from AUTOLAB (Eco Chemie BV) which worked in the amperostatic mode, and was controlled by the EAS v. 2 software (Eco Chemie BV).

Results and discussion

UV-VIS and IR investigations

UV-VIS spectra of the ligands and their $\text{Ag}(\text{II})$ complex solutions ($c = 1 \times 10^{-3} \text{ mol dm}^{-3}$) within the range 200–800 nm were recorded. A typical spectrum is shown in Figure 1.

The results of the UV-VIS measurements are presented in Table 1. The symbols λ_1 and λ_2 refer to the absorption maximum of the charge-transfer and $d-d$ transitions, respectively. Table 1 also includes values of the absorption maxima λ_1 and λ_2 for the $\text{Ag}(\text{cyclam})^{2+}$ complex [12] which will be used in further discussion.

All UV-VIS spectra indicate that aqueous solutions of the Ag^{2+} cation (d^9) with the following ligands: *isocyclam*, *scorpiand*, *trans*- $\text{Me}_2[14]\text{anN}_4$ *cis*- $\text{Me}_6[14]\text{anN}_4$, and *(N-Me)Me_2py[14]anN_4*, contain complexes with a N_4 square-plane coordination centre due to the presence of a band $\lambda_2 = 348\text{--}376 \text{ nm}$ arising from the $b_{1g} \rightarrow b_{2g}$ transition in the field of the ligand with D_{4h} symmetry [12].

The absorption maximum differences of the $d-d$ transition (λ_2) between $\text{Ag}(\text{cyclam})^{2+}$ and the other $\text{Ag}(\text{II})$ complexes can be explained in the following manner. In the

Table 1. UV-VIS measurements; λ_1 and λ_2 in nm, ϵ_1 and ϵ_2 in $\text{cm}^{-1} \text{ mol}^{-1} \text{ dm}^{-3}$.

Compound	$\lambda_1(\epsilon_1)$	$\lambda_2(\epsilon_2)$
$\text{Ag}(\text{cyclam})^{2+}$ [12]	280 (3.39×10^3)	350 (6.39×10^3)
$\text{Ag}(\text{isocyclam})^{2+}$	276 (2.13×10^3)	374 (3.29×10^3)
$\text{Ag}(\text{scorpiand})^{2+}$	286 (2.68×10^3)	376 (4.92×10^3)
$\text{Ag}(\text{trans-Me}_2[14]\text{anN}_4)^{2+}$	282 (2.18×10^3)	348 (3.95×10^3)
$\text{Ag}(\text{cis-Me}_6[14]\text{anN}_4)^{2+}$	282 (7.10×10^2)	352 (1.42×10^3)
$\text{Ag}((\text{N-Me})\text{Me}_2\text{py}[14]\text{anN}_4)^{2+}$	283 (2.43×10^3)	365 (4.33×10^3)

spectrum of the $\text{Ag}(\text{scorpiand})^{2+}$ complex the shift of the absorption maximum ($\lambda_2 = 376 \text{ nm}$), in comparison to the spectrum of $\text{Ag}(\text{cyclam})^{2+}$ ($\lambda_2 = 350 \text{ nm}$), may be caused by the presence of nitrogen substituted by the electrodonor 1-aminoethyl group. It slightly increases the basicity of that atom and the covalence of the Ag-N bond as well. Thus, in the $\text{Ag}(\text{scorpiand})^{2+}$ complex the difference of the energy of the central ion levels b_{1g} and b_{2g} is lower than in the $\text{Ag}(\text{cyclam})^{2+}$ complex and the value of this complex has a higher wavelength than for the $\text{Ag}(\text{cyclam})^{2+}$ complex.

The difference in the absorption maximum of the $\text{Ag}(\text{cyclam})^{2+}$ and $\text{Ag}(\text{isocyclam})^{2+}$ complexes may be explained in terms of non-equal coordination sites in these complexes. In the $\text{Ag}(\text{isocyclam})^{2+}$ complex the non-symmetrical position of the nitrogen donor atoms in the xy plane causes an increase of the d_{xy} orbital energy (b_{2g} level) and a decrease of the $d_{x^2-y^2}$ orbital energy (b_{1g} level) of the central ion. This causes a decrease of the differences in energy between those levels and thus decreasing the absorption maximum. The same situation was observed in the case of $\text{Ni}(\text{II})$ low-spin complexes with those ligands. The absorption maximum of $\text{Ni}(\text{cyclam})^{2+}$ was at 445 nm [22] and at 463 nm for $\text{Ni}(\text{isocyclam})^{2+}$ [17].

In the case of the $\text{Ag}((\text{N-Me})\text{Me}_2\text{py}[14]\text{anN}_4)^{2+}$ complex there is an overlap of the two opposite effects affecting the absorption maximum of the $d-d$ transition. In comparison with *isocyclam*, in the *(N-Me)Me_2py[14]anN_4* molecule there is one nitrogen atom with lower basicity (the nitrogen atom of the pyridine moiety causes a hypsochromic shift) and one nitrogen atom with a higher basicity (the methyl substituted nitrogen atom causes a bathochromic shift). Due to the almost identical absorption maxima in the spectra of $\text{Ag}((\text{N-Me})\text{Me}_2\text{py}[14]\text{anN}_4)^{2+}$ and $\text{Ag}(\text{isocyclam})^{2+}$ one can conclude that both effects are comparable.

In comparison with $\text{Ag}(\text{cyclam})^{2+}$, the presence of the methyl substituents in the molecules of *trans*- $\text{Me}_2[14]\text{anN}_4$ and *cis*- $\text{Me}_6[14]\text{anN}_4$, which are not bonded to the nitrogen donor atom, do not affect the UV-VIS spectra of the $\text{Ag}(\text{II})$ complexes with these ligands. The absorption maxima of the $d-d$ transition of these compounds are almost the same.

The first band in the UV-VIS spectra arises from the charge-transfer transition (λ_1). This band is connected with the partial inner oxidation of the ligand by the central ion. The lower the absorption maximum of this band, the lower is the ability to undergo inner red-ox process in the metal-

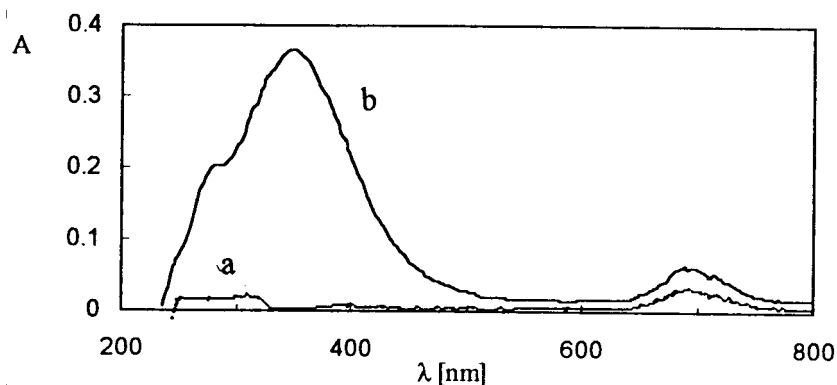


Figure 1. UV-VIS spectra of (a) the *trans*-Me₂[14]anN₄ ligand ($c = 1 \times 10^{-3}$ mol dm⁻³), (b) the Ag(*trans*-Me₂[14]anN₄)²⁺ complex ($c \approx 1 \times 10^{-3}$ mol dm⁻³); $\mu = 0.1$ (KNO₃), $T = 298$ K.

ligand system followed by decomposition of the silver(II) complex.

In all UV-VIS spectra of the Ag(II) complexes under investigation the absorption maximum of this band is nearly equal (Table I) and we can conclude, that the stabilization in these compounds is almost the same.

The UV-VIS spectra of the Ag(*cyclam*)²⁺ and Ag(*scorpiand*)²⁺ complexes are almost the same (Table I). There is an absorption band characteristic for square-planar complexes of Ag(II): for Ag(*cyclam*)²⁺ $\lambda_2 = 350$ nm; for Ag(*scorpiand*)²⁺ $\lambda_2 = 376$ nm. Moreover, the IR spectrum of the solid Ag(*scorpiand*)(NO₃)₂ complex (KBr) shows bands at $\nu = 3450$ cm⁻¹ and $\nu = 1620$ cm⁻¹ which are characteristic for primary amines. This proves that the nitrogen atom of the —CH₂—CH₂—NH₂ group both in the aqueous solution and in the solid state does not participate in the coordination of the Ag²⁺ ion. Thus, in contrast to the Ni(*scorpiand*)²⁺ complex [18], it is not possible to obtain a five-coordinate tetragonal-pyramidal complex of Ag(II) with *scorpiand*. In addition, the UV-VIS spectra of the Ag(*scorpiand*)²⁺ complex solutions did not change within the pH range 2.50–7.50 and no new absorption bands appeared which could be due to the formation of different complex forms.

Potentiometric measurements

Potentiometric measurements were used to determine the stability constant of the silver(I) complex with py[12]anN₄ with a M:L ratio of 1:1. The value of the stability constant was calculated using a curve fitting computer program using Newton–Raphson's method to solve the mass balance equations system. The calculated value of the stability constant is: $\log \beta_{01} = 6.00 \pm 0.1$; $T = 298$ K, $\mu = 0.1$ (KNO₃).

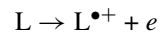
Voltammetric measurements

In order to determine the formal potential of the Ag(II)/Ag(I) system in the presence of the ligands under investigation and to describe the mechanism of the electroreduction of the silver(II) complexes with these ligands on a platinum electrode in aqueous solution the staircase and linear cyclic voltammetry methods were used.

Voltammograms of the 1×10^{-3} mol dm⁻³ ligands solutions and of the 1×10^{-3} mol dm⁻³ AgL(NO₃)₂ complex solutions within the potential range $E = -1000$ – 1000 mV were recorded with a potential sweep rate of 10 – 100 mV s⁻¹. The Analysis/Peak Search function of the GPES v. 4.5 program allowed determination of the peak potential and current peak with an accuracy of ± 1 mV and ± 0.1 μ A, respectively.

The identification of the peaks corresponding to the following electrode processes was made according to previously reported methods [11–14, 16].

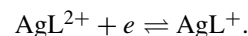
The voltammetric curves of the ligands had shown only one peak within the range 500–800 mV arising from irreversible ligand oxidation



The most probable product of this reaction was radical cation $L^{\bullet+} + e$ which initiated the polymerization reaction. Thus, a nonconducting polymer with unknown constitution was formed, covering the working electrode surface. For each of the complexes only three scans were made. During the following scans the surface of the working electrode was covered by a nonconducting film which was the product of the radical electropolymerization of the free ligands.

Typical voltammetric curves of *isocyclam* (Figure 2, curve 1), the Ag(*isocyclam*)²⁺ complex (Figure 2, curve 2) and *cis*-Me₆[14]anN₄ (Figure 3, curve 1) and the Ag(*cis*-Me₆[14]anN₄)²⁺ complex (Figure 3, curve 2) are presented.

On the voltammograms of the AgL²⁺ complexes (L = *isocyclam*, *scorpiand*, (*N*-Me)Me₂py[14]anN₄) apart from the peak of NO₃⁻ ion reduction (A), the region of water oxidation (B), the peak of uncomplexed Ag⁺ ion reduction (C), the peak of metallic silver oxidation (D) and the peak of the free ligand oxidation (E) there are also peaks F and G. These two peaks refer to the coupling redox system. Narrowing of the potential range in the cathodic part of the CVA curve to a potential higher than E_G caused disappearance of peak F (Figure 2, curve 3). Thus, as in [11–13], peaks F and G refer to the redox system:



On the voltammetric curves of the AgL²⁺ complexes (L = *isocyclam*, *scorpiand*, (*N*-Me)Me₂py[14]anN₄) the po-

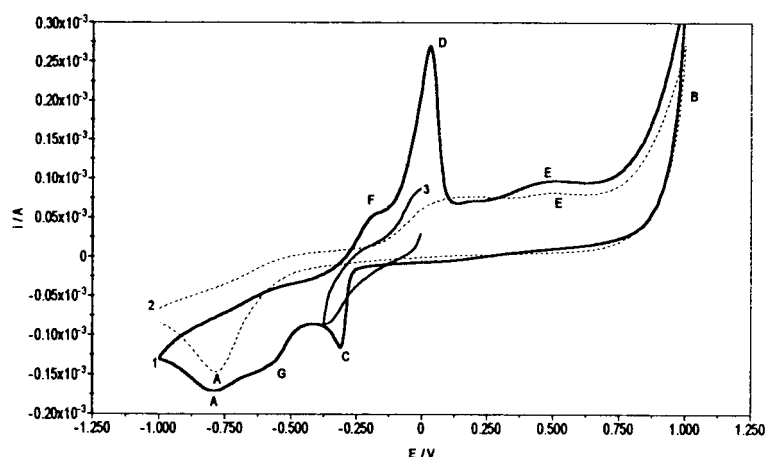


Figure 2. Cyclic voltammograms of (1) *isocyclam*, $c = 1 \times 10^{-3} \text{ mol dm}^{-3}$, (2) the $\text{Ag}(\textit{isocyclam})^{2+}$ complex, $c \approx 1 \times 10^{-3} \text{ mol dm}^{-3}$; (3) the $\text{Ag}(\textit{isocyclam})^{2+}$ complex, $c \approx 1 \times 10^{-3} \text{ mol dm}^{-3}$; curves recorded in the potential range -375 to 0 mV. Rate of potential sweep $\nu = 50 \text{ mV s}^{-1}$, potentials vs. $\text{Ag}^0 \mid 0.01 \text{ mol dm}^{-3} \text{ AgNO}_3 + 0.09 \text{ mol dm}^{-3} \text{ KNO}_3$; $\mu = 0.1$ (KNO_3).

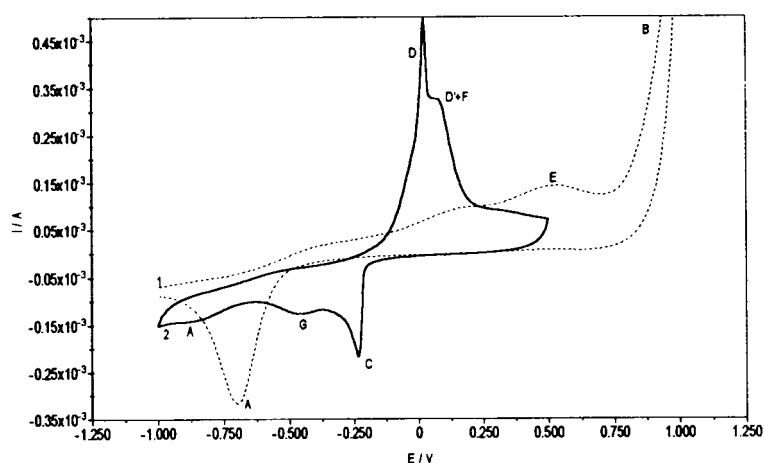


Figure 3. Cyclic voltammograms of (1) *cis*- $\text{Me}_6[14]\text{anN}_4$, $c = 1 \times 10^{-3} \text{ mol dm}^{-3}$; (2) the $\text{Ag}(\textit{cis}\text{-Me}_6[14]\text{anN}_4)^{2+}$ complex, $c \approx 1 \times 10^{-3} \text{ mol dm}^{-3}$; rate of potential sweep $\nu = 50 \text{ mV s}^{-1}$, potentials vs. $\text{Ag}^0 \mid 0.1 \text{ mol dm}^{-3} \text{ AgNO}_3 + 0.09 \text{ mol dm}^{-3} \text{ KNO}_3$ $\mu = 0.1$ (KNO_3).

tential peak *F* was lower than the potential peak of the metallic silver oxidation *D*. Moreover, the peak current ratio I_{pc}/I_{pa} for these $\text{Ag}(\text{II})/\text{Ag}(\text{I})$ redox systems is greater than 1 (Table 2). The lower value of the anodic peak current compared to the cathodic value is due to the disproportionation of the $\text{Ag}(\text{I})$ complexes [11–13, 16]. Thus, the concentration of the silver(I) complexes was reduced and a lower anodic peak current was observed. The value of the I_{pc}/I_{pa} ratio also shows that the rate of the disproportionation process is the biggest for the $\text{Ag}(\textit{isocyclam})^{2+}$ complex. However, for the $\text{Ag}(\textit{scorpiand})^{2+}$ and $\text{Ag}((N\text{-Me})\text{Me}_2\text{py}[14]\text{anN}_4)^{2+}$ complexes the rates of these processes are comparable.

However, on the voltammetric curves of the AgL^{2+} complexes ($L = \textit{trans}\text{-Me}_2[14]\text{anN}_4$, *cis*- $\text{Me}_6[14]\text{anN}_4$) (Figure 3), potential peak *F* is higher than potential peak *D* and overlaps peak *D'* connected with desorptive oxidation of metallic silver. In this case, after narrowing the potential range in the cathodic part of the CVA curve to $E > E_G$, the current of the *D' + F* peak decreased. However, the current of the *D'* peak was not reproducible. Thus, it was not possible to determine the current peak of the silver(I) complexes oxidation, and consequently, there are no values of

Table 2. Electrochemical characteristics of the $\text{AgL}^{2+/+}$ redox system in the presence of ligands 1–5; the potentials are given vs. $\text{Ag}^0 \mid 0.01 \text{ mol dm}^{-3} \text{ AgNO}_3 + 0.09 \text{ mol dm}^{-3} \text{ KNO}_3$ ($\nu = 50 \text{ mV s}^{-1}$).

	1	2	3	4	5
E_{pa} (mV)	−199	146	80.0	−200	−252
E_{pc} (mV)	−558	−531	−469	−535	−540
ΔE_{pac} (mV)	359	677	549	335	288
I_{pa} (μA)	12.0	–	–	16.4	20.7
I_{pc} (μA)	18.2	3.79	15.0	18.1	23.0
I_{pc}/I_{pa} (–)	1.52	–	–	1.12	1.11

the anodic current peak for these complexes in Table 2. The electrochemical characteristics of the $\text{Ag}(\text{II})/\text{Ag}(\text{I})$ redox system in the presence of *isocyclam*, *scorpiand*, *trans*- $\text{Me}_2[14]\text{anN}_4$, *cis*- $\text{Me}_6[14]\text{anN}_4$, $(N\text{-Me})\text{Me}_2\text{py}[14]\text{anN}_4$ are presented in Table 2.

For the $\text{Ag}(\text{py}[12]\text{anN}_4)^+$ complex, according to the results presented in the synthesis of the silver(II) complexes section, no oxidation peak of this complex was observed on

the voltammetric curves. Thus, the formation of the Ag(II) complex with this ligand is not possible

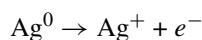
Values of $\Delta E_{\text{pac}} > 160$ mV (Table 2) show that the Ag(II)/Ag(I) redox system in the presence of *scorpiand*, *isocyclam*, *trans*-Me₂[14]anN₄, *cis*-Me₆[14]anN₄ and (*N*-Me)Me₂py[14]anN₄ is electrode irreversible. Thus, estimation of the formal potential values on the basis of voltammetric measurements is not possible. However, it is possible to determine the E_f^0 of these redox systems by amperostatic coulometry measurements.

Amperostatic coulometry measurements

The aim of the amperostatic coulometry measurements was to determine the formal potential of the Ag(II)/Ag(I) system in the case when the Ag(II) complex electroreduction process was electrode irreversible or when the rate of the Ag(I) complexes disproportionation, which are the product of the Ag(II) complexes electroreduction, was slow on the time scale of the voltammetric measurements.

In order to definitely oxidize the silver(I) complexes the electrooxidation was carried out ($i = 0.5$ mA) until maximum EMF was obtained. After that, electroreduction of the Ag(II) complexes was made under amperostatic conditions. During electroreduction currents of 0.5, 1.0 and 1.5 mA were applied. The process was ended when the solution was colourless. It was showed that all the Ag(II) complex was reduced.

Two kinds of EMF = $f(t) = f(Q)$ curves were obtained. In the first type of curve there was a potential minimum and the potential increase of the system with advancing reduction processes. It is noteworthy that at $E < 0$ mV vs. Ag⁰ | 0.01 mol dm⁻³ AgNO₃ + 0.09 mol dm⁻³ KNO₃, metallic silver was deposited on the Pt electrode. This kind of curve was obtained in the case of the Ag(*isocyclam*)²⁺ complex electroreduction (Figure 4). Moreover, the shape of this curve was independent of the value of the applied current. The relationship obtained distinctly points to the presence of two redox systems. Taking into consideration the CVA curves, which point to the potential regions of the occurring processes, one can conclude with a high probability, that we are dealing with reduction of the AgL²⁺ complex in the descending part of the coulometric curves and with oxidation of metallic silver resulting from disproportionation of the AgL²⁺ complex. The formal potential of the system:

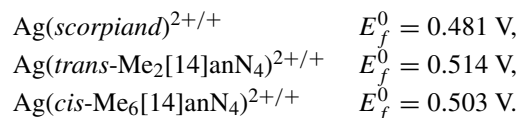


is higher than the formal potential of the Ag(II)/Ag(I) system in the presence of *isocyclam* [11, 12]. The increase of the potential may be also caused by the increase of the Ag(II) complex concentration, which is the product of the Ag(I) complex disproportionation. This indicated that the rate of the Ag(II)-*isocyclam* complex electroreduction and the rate of the Ag(I)-*isocyclam* complex disproportionation were comparable. It is in agreement with the CVA measurement results, where in the case of *isocyclam*, the current peak ratio $I_{\text{pc}}/I_{\text{pa}} = 1.55$ was the largest. The occurrence of the two redox systems in solution was the reason for

the high rate of the Ag(I)-*isocyclam* complex disproportionation. Thus, determination of the formal potential of the Ag(II)/Ag(I) system in the presence of *isocyclam* was not possible.

On the second kind of EMF = $f(t) = f(Q)$ curves a potential minimum was not observed. Such curves were obtained in the case of the Ag(II) complexes with *scorpiand*, *trans*-Me₂[14]anN₄, *cis*-Me₆[14]anN₄ and (*N*-Me)Me₂py[14]anN₄ electroreduction, where the peak current ratio $I_{\text{pc}}/I_{\text{pa}}$ was *ca.* 1.1 and the disproportionation rate was considerable lower. The example of this type of curve is presented in Figure 4. The shape of this curve is like the shape of a typical redox titration curve. Thus, the values of the redox systems formal potential were determined using the 1st derivative method from $\partial \text{EMF}/\partial t$ curves.

Consequently, it was possible to determine the formal potential value for the following Ag(II)/Ag(I) redox systems (potentials vs. NHE):



On the basis of electrochemical investigations one can conclude that thermodynamic stabilization of Ag(II) in the presence of *scorpiand*, *trans*-Me₂[14]anN₄ and *cis*-Me₆[14]anN₄ is more diverse. Among these three complexes the highest stabilization, i.e., the lowest value of the formal potential of the Ag(II)/Ag(I) redox system, occurs in the case of the Ag(*scorpiand*)^{2+/+} redox system. The likely reason is the presence of the one *N*-substituted nitrogen donor atom in the *scorpiand*'s ring possessing higher basicity than the nitrogen atoms in the *trans*-Me₂[14]anN₄ and *cis*-Me₆[14]anN₄ molecules. However the pyridine moiety in (*N*-Me)Me₂py[14]anN₄ causes significant reducing stabilisation of the Ag²⁺ ion.

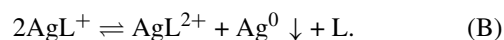
The mechanism of the reduction of the silver(II) complexes

On the basis of CVA and amperostatic coulometry measurements we can propose the following mechanism of the reduction of the silver(II) complexes that occurs on the platinum electrode in aqueous solution.

In the first step the silver(II) complex is irreversibly reduced to the silver(I) complex:

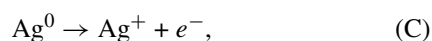


The product of this reaction, the silver(I) complex, undergoes the disproportionation process to the silver(II) complex and metallic silver is deposited on the working electrode:



Thus, this process occurs according to the EC mechanism.

At the silver(II) complex reduction potential the following Ag(I)/Ag(0) redox system is formed:



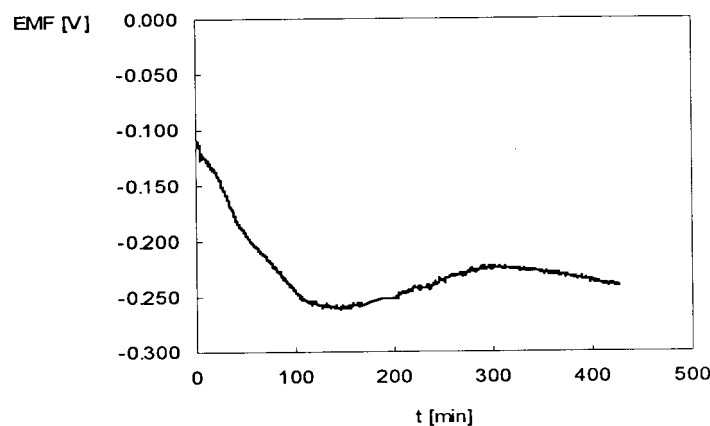


Figure 4. Amperostatic reduction curve of the $c \approx 1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Ag(isocyclam)}^{2+}$ aqueous solution; $i = 0.5 \text{ mA}$, $T = 298 \text{ K}$, $\mu = 0.1 \text{ (KNO}_3\text{)}$.

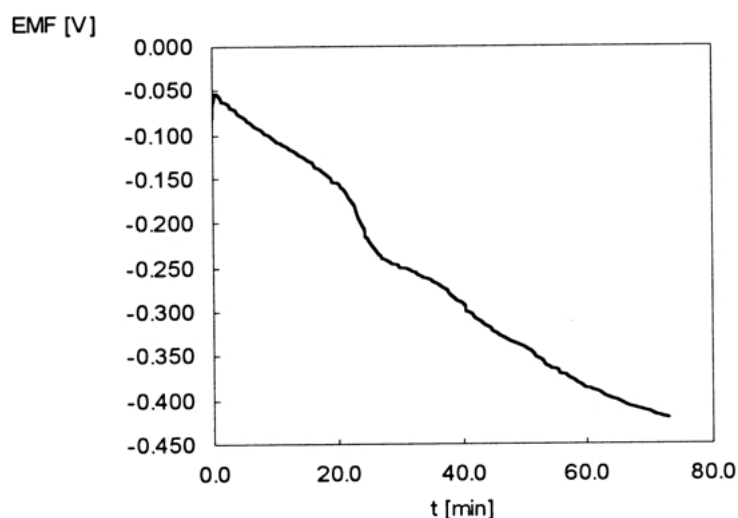
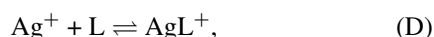


Figure 5. Amperostatic reduction curve of the $c \approx 1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Ag(scorpian)}^{2+}$ aqueous solution; $i = 1.5 \text{ mA}$, $T = 298 \text{ K}$, $\mu = 0.1 \text{ (KNO}_3\text{)}$.

which has a formal potential higher than the $\text{AgL}^{2+/+}$ redox system. Hence, disproportionation process (B) is thermodynamically reasonable. Then, silver(I) in the presence of free ligand L forms the silver(I) complex:



which again undergoes disproportionation to the silver(II) complex and metallic silver (B).

References

1. K.B. Yatsimirskii: *Zh. Neorg. Khim.* **36**, 2010 (1991); *Chem. Abstr.* **115**, 221611v (1991).
2. P. Urbaniak, J. Dziegieć and A. Grzejdzia: *Russ. J. Coord. Chem.* **20**, 455 (1994).
3. S. Domagała, J. Dziegieć and A. Grzejdzia: *Russ. J. Coord. Chem.* **21**, 803 (1995).
4. D. Sroczynski, J. Dziegieć and A. Grzejdzia: *Russ. J. Coord. Chem.* **23**, 447 (1997).
5. K. Henrick, P.A. Tasker and L.F. Lindoy: *Prog. Inorg. Chem.* **33**, 3 (1985).
6. E. Suet, A. Laouenan, H. Handel and R. Guglielmetti: *Helv. Chim. Acta* **67**, 441 (1984).
7. M.O. Kestner and A.L. Allred: *J. Am. Chem. Soc.* **94**, 7189 (1972).
8. E.K. Barefield and M.T. Mocella: *Inorg. Chem.* **12**, 2829 (1973).
9. L.U. Tolentino and H.N. Po: *J. Coord. Chem.* **13**, 341 (1984).
10. M. Pesavento, A. Profumo, T. Soldi and L. Fabbri: *Inorg. Chem.* **24**, 3873 (1985).
11. A. Grzejdzia: *Polish. J. Chem.* **67**, 2133 (1993).
12. A. Grzejdzia: *Monatsh. Chem.* **125**, 107 (1994).
13. A. Grzejdzia: *Polish. J. Chem.* **68**, 1223 (1994).
14. B. Olejniczak, A. Grzejdzia and J. Dziegieć: *Monatsh. Chem.* **128**, 13 (1997).
15. D. Sroczynski and A. Grzejdzia: *36th Congress Geneva 1997*, poster SB-I 17, *Chimia* **51**, 432 (1997).
16. A. Grzejdzia: *Polish. J. Chem.* **68**, 1395 (1994).
17. L. Sabatini and L. Fabbri: *Inorg. Chem.* **18**, 438 (1979).
18. P.S. Pallavicini, A. Perotti, A. Poggi, B. Seghi and L. Fabbri: *J. Am. Chem. Soc.* **109**, 5139 (1987).
19. W.G. Thorpe and J.K. Kochi: *J. Inorg. Nucl. Chem.* **33**, 3958 (1971).
20. H.L. Suprenant, T.H. Ridgway and C.N. Reilly: *J. Electroanal. Chem.* **75**, 125 (1977).
21. M. Seralathan, R.A. Osteryoung and J.G. Osteryoung: *J. Electroanal. Chem.* **222**, 69 (1987).
22. L. Fabbri: *Inorg. Chem.* **16**, 2667 (1977).

