Investigations on Equilibria between Ag(I) and Tetraazacyclic Amines in Dimethylsulfoxide

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Summary. The formation constants of complexes of Ag(I) with 1,4,8,11-tetraazacyclotetradecane (*TACT*), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (*TMTACT*), and 1,4,8,12-tetraazacyclopentadecane (*TACP*) as well as equilibrium constants of the disproportionation of Ag($TACT$)$^+$ and Ag($TACP$)$^+$ in dimethylsulfoxide have been determined by spectrophotometry and potentiometry. Ag(II) complexes of the same amines have also been characterized by spectrophotometry. The mechanism of the electrode processes of the complexes under investigations has been elucidated by voltammetric and coulometric methods; formal potentials of the redox systems have been determined.

Keywords. Chronovoltammetry; Coulometry; Redox systems; Silver complexes; Tetraazamacrocyclic ligands.

Untersuchungen der Gleichgewichte zwischen Ag(I) und tetraazacyclischen Aminen in Dimethylsulfoxid

Zusammenfassung. Die Bildungskonstanten von Komplexen zwischen Ag(I) und 1,4,8,11-Tetra-azacyclotetradecan (*TACT*), 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecan (*TMTACT*) und 1,4,8,12-Tetraazacyclopentadecan (*TACP*) sowie die Gleichgewichtskonstanten der Dispropor-tionierungsreaktion von Ag($TACT$)$^+$ und Ag($TACP$)$^+$ wurden in Dimethylsulfoxid spektrophoto-metrisch und potentiometrisch ermittelt. Ag(II)-Komplexe derselben Amine wurden ebenfalls spektrophotometrisch charakterisiert. Der Mechanismus der Elektrodenprozesse der untersuchten Komplexe wurde mittels voltammetrischer und coulometrischer Methoden aufgeklärt; die formalen Potentiale der Redoxsysteme wurden bestimmt.

Introduction

The process of disproportionation of Ag(I) ions in the presence of tetraazacyclic amines involving the precipitation of metallic silver and formation of Ag(II) complexes has been known for twenty years [1, 2]:

$$2\,\mathrm{Ag}^+ + L \rightleftarrows \mathrm{Ag}L^{2+} + \mathrm{Ag}^0 \qquad (1)$$
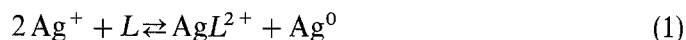
This process occurs when the "bonding cavity" available for a metal ion in the ligand molecule is large enough for the coordination of Ag^{2+}, but too small to form four planar Ag(I)–N bonds. *Clarck* and *Harrowfield* [3] have examined the disproportionation process and concluded that it is irreversible in acetone and methanol, irreversible to a great extent in *DMF*, and practically absent in *DMSO* and acetonitrile.

Our previous studies on silver complexes with saturated tetraazacyclic amines in water, acetonitrile, and propylene carbonate indicated that the best stabilization of Ag^{2+} ions occurs in the case of 1,4,8,12-tetraazacyclopentadecane (*TACP*) and, to lesser extent, for 1,4,8,11-tetraazacyclotetradecane (*TACT*) and 1,4,8,11-tetra-methyl-1,4,8,11-tetraazacyclotetradecane (*TMTACT*) [4–7]. The disproportionation does not take place for investigated complexes in acetonitrile, but, in contrast to the experimental results [3], theoretical considerations point at the possibility of this process in *DMSO* [7]. Hence, it was interesting to investigate the above systems in this solvent.

Results and Discussion

Spectrophotometric investigations

In the case of *TACP* and *TACT* the UV/Vis spectrum exhibits two absorption maxima. One of them (λ_1) corresponds to the charge transfer transition between ligand and metal ion; the another one (λ_2) is ascribed to the $b_{2g} \rightarrow b_{1g}$ transition, typical for a d^9 ion in D_{4h} symmetry. The found values of molar absorptivity were considerably lower than those obtained for the solutions of all complexes in water (including $Ag(TMTACT)^{2+}$) [2] and in *DMSO*. For $Ag(TMTACT)^{2+}$, an additional weak absorption maximum was recorded at $\lambda_3 = 688$ nm; in this case, a decrease of absorptivity at λ_2 and an increase at λ_3 vs. time was observed. The spectrophotometric characteristics of the compounds are given in Table 1.

Potentiometric investigations

The values of molar absorptivity of $Ag(TACP)^{2+}$ and $Ag(TACT)^{2+}$ in *DMSO* in comparison with ε values for the solutions of these compounds prepared in water and transferred to *DMSO* show that disproportionation of Ag(I) ions in the presence of the investigated ligands in *DMSO* occurs to a considerably less extent. Preliminary voltammetric measurements demonstrated the presence of a reduction peak of the Ag(I) complexes. In the equilibrium state, we deal with the presence of AgL^+ and AgL^{2+}; hence, the disproportionation in *DMSO* proceeds according to Eq. (2):

$$2\,AgL^+ \rightleftarrows Ag^0 + AgL^{2+} + L \tag{2}$$
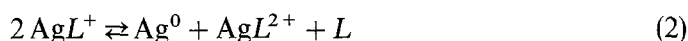
The determination of the equilibrium constant for this disproportionation by potentiometric methods alone [4, 5] is impossible. The equilibria established in the
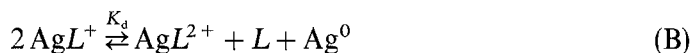
Table 1. Spectrophotometric characteristics of Ag(II) complexes

	ε	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)
Ag(*TACT*(ClO$_4$)$_2$)	1880	330	412	–
Ag(*TACP*(ClO$_4$)$_2$)	2510	302	374	–
Ag(*TMTACT*(ClO$_4$)$_2$)	710	310	402	688

investigated solutions can be described by the following equations:

$$Ag^+ + L \overset{\beta}{\rightleftarrows} AgL^+ \tag{A}$$

and

$$2\,AgL^+ \overset{K_d}{\rightleftarrows} AgL^{2+} + L + Ag^0 \tag{B}$$

Therefore, the values of the formation constant (β) and the disproportionation constant (K_d) can be determined *via* the respective concentrations of AgL^{2+} (c_{II}, spectrophotometry) and AgL^+ (c_I, potentiometry):

$$K_d = \frac{c_{II}(c_L^0 - c_{Ag^+}^0 + c_{II} + c_{exp})}{(c_{Ag^+}^0 - 2c_{II} - c_{exp})} \quad \text{and} \quad \beta = \frac{c_{Ag^+}^0 - 2c_{II} - c_{exp}}{c_{exp}(c_L^0 - c_{Ag^+}^0 + c_{II} + c_{exp})}$$

(c_L^0: initial concentration of the ligand; $c_{Ag^+}^0$: initial concentration of Ag^+ ions; c_{exp}: equilibrium concentration of Ag^+ ions, obtained from potentiometric measurements; $c_I = c_{Ag^+}^0 - 2c_{II} - c_{exp}$).

Potentiometric measurements (EMF value) were carried out for the following cell: $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)$ $\|0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)\|$ $c_{Ag^+}^0$ $(DMSO) + c_L^0$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)|Ag^0$. The *Nernst* equation for the Ag^+ ions ($AgClO_4$ in *DMSO*) was satisfied within the concentration range from 10^{-6} to $10^{-2}\,M$ with a slope 59.29 ± 0.1 mV.

The measurements were carried out by the "out of cell" method; c_L^0 and $c_{Ag^+}^0$ ranged from 10^{-3} to $3 \times 10^{-3}\,M$ in the case of *TACP* and from 5×10^{-4} to $7 \times 10^{-4}\,M$ for c_L^0 and from 5×10^{-4} to $1.5 \times 10^{-3}\,M$ for $c_{Ag^+}^0$ in the case of *TACT*(*TACT* is slightly soluble in *DMSO*). The processes proceeded slowly, and stable EMF values for the investigated systems were obtained after 3 days (all solutions were light protected). The results of the measurements and the disproportionation formation constant values are given in Table 2.

In contrast to *TACT* and *TACP*, *TMTACT* forms stable complexes of the composition AgL^+ in *DMSO*. Formation constant and composition were determined by potentiometric titration of *TMTACT* within the concentration range of $c_L^0 = 10^{-2}$–$10^{-3}\,M$ with 10^{-2}–$10^{-1}\,M$ $AgClO_4$ solutions in *DMSO*. The ligand concentration was additionally verified using the potential drop in the titration curve at $c_L^0/c_{Ag^+}^0 = 1$. The value of the formation constant was determined nummerically according to the least-squares program Miniquad [9]. A typical titration curve is shown in Fig. 1. For Ag(*TMTACT*)$^+$, $\log\beta = 7.84 \pm 0.1$ (average square deviation: 0.2 mV).

Voltammetric and coulometric measurements

In order to investigate the redox systems in the Ag(II) complex solutions and to examine the mechanisms of the electrode processes involved, chronovoltammetric and coulometric measurements were carried out in the system $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)\|0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)\|$ test sample $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)|Pt$. Voltammograms were

Table 2. Results of potentiometric and spectrophotometric measurements of the disproportionation processes for $Ag(TACT(ClO_4)_2)$ and $Ag(TACP(ClO_4)_2)$ in $DMSO$; $T = 298$ K, EMF vs $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)$, $\mu = 0.1$ $((C_2H_5)_4NClO_4)$

|	$c^0_{Ag^+}$ $(\times 10^3\,M)$	c^0_L $(\times 10^3\,M)$	EMF (mV)	c_{II} $(\times 10^3\,M)$	c_I $(\times 10^4\,M)$	$\log\beta$	$\log K$
	1.5	1.5	−166.6	0.645	1.945	4.28	1.05
	2.0	1.0	−113.7	0.910	0.591	4.20	0.91
TACP	2.8572	1.4286	−110.0	1.320	0.777	4.25	0.83
	3.0	1.5	−108.5	1.385	0.821	4.23	0.83
	3.0	3.0	−167.5	1.280	4.250	4.34	0.96
	$c^0_{Ag^+}$ $(\times 10^3\,M)$	c^0_L $(\times 10^4\,M)$	EMF (mV)	c_{II} $(\times 10^4\,M)$	c_I $(\times 10^4\,M)$	$\log\beta$	$\log K$
	1.3793	6.8967	−83.9	4.25	1.448	3.50	0.39
	1.0	5.0	−81.8	2.25	1.328	3.35	0.26
TACT	0.75	7.5	−104.1	2.00	1.745	3.42	0.39
	0.50	5.0	−106.2	1.15	1.083	3.38	0.43
	1.50	7.5	−83.1	4.75	1.533	3.50	0.39
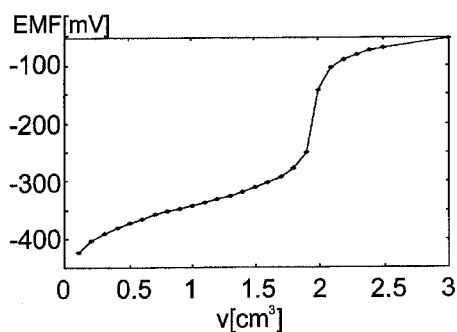
Fig. 1. Potentiometric titration curve of $40\,cm^3$ $4.9 \times 10^{-3}\,M$ $TMTACT$ solution with $0.1\,M$ $AgClO_4$ solution in $DMSO$; EMF vs. $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)$, $\mu = 0.1$ $((C_2H_5)_4NClO_4)$, $T = 298$ K

recorded at scan rates of 10–100 mV/s within a potential range of $E = -1000$ to $+1000\,mV$ vs. an $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)$ electrode. In coulometric measurements, the examined solutions were oxidized and reduced amperostatically at $i = 1\,mA$.

Examination of Ag(II)/Ag(I)-TACP and Ag(II)/Ag(I)-TACT systems

The following voltammograms were recorded: 1) $2 \times 10^{-3}\,M$ solution of ligand and 2) $2 \times 10^{-3}\,M$ $Ag^+ + 2 \times 10^{-3}\,M$ $TACP$ solution in equilibrium state (after 3 days). In the region $E > 400\,mV$, the ligand solution voltammogram shows irreversible oxidation of $TACP$ with an anodic peak at $E \sim +650\,mV$. In subsequent cycles, the height of anodic peak decreases, whereas at the same time a film of unidentified

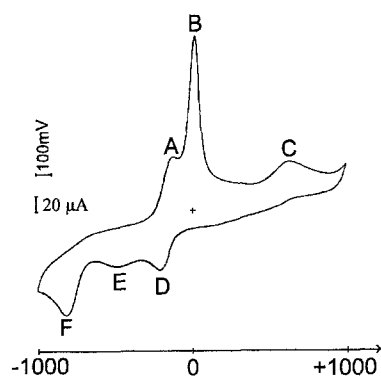Fig. 2. Voltammogram of $2 \times 10^{-3} M$ $Ag^+ + 2 \times 10^{-3} M$ $TACP$ solution in $DMSO$ in the equilibrium state; $v = 50\,mV/s$, E vs. $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)$, $\mu = 0.1\,((C_2H_5)_4NClO_4)$, $T = 298\,K$

composition, insoluble in $DMSO$, can be observed at the electrode. The curve of solution 2 (Fig. 2), except of the anodic peak of ligand oxidation, demonstrates a reversible redox system:

$$Ag(TACP)^{2+} + e \rightleftarrows Ag(TACP)^+ \qquad (I)$$

(the pair of peaks at $E_a \sim -140\,mV$ (A) and $E_c \sim -210\,mV$ (D)) and two cathodic peaks E and F. Upon increasing of the $TACP$ concentration to $5 \times 10^{-3} M$, the cathodic peak E dissappeared, whereas peak F increased. This phenomenon proves a shift of the complexing equilibrium in solution towards the product side. Hence, it can be stated that peaks E and F are connected with the reduction of Ag^+ ions and of complex $Ag(TACP)^+$, respectively. The corresponding characteristic desorption peak of metallic silver oxidation (B) can be found at $E \sim +50\,mV$. Narrowing the potential range ($E = -350$ to $+200\,mV$) causes the decrease of its height, but this peak is permanently present, including the case when the reduction of Ag(I) compounds does not occur. The same phenomenon, confirming the disproportionation of the $Ag(TACP)^+$ complex, was observed in H_2O and PC [4,6]. The CVA curve taken within the potential range $E = -350$ to $+50\,mV$ allows to determine the value of formal potential for the above system ($E_f^0 = -177 \pm 3\,mV$ vs. $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)$ electrode; $+93\,mV$ vs. SHE [10].

In the case of $TACT$, the following voltammograms were recorded: 1) $7.5 \times 10^{-4} M$ $TACT$ solution, 2) $7.5 \times 10^{-4} M$ $Ag^+ + 7.5 \times 10^{-4} M$ $TACT$ solution in equilibrium state (after 3 days), 3) $10^{-3} M$ $Ag(TACT(ClO_4)_2)$ solution, synthesized in water and transferred to $DMSO$. The CVA curve of the $TACT$ solution indicates an irreversible oxidation of the ligand for $E > +500\,mV$ with an anodic peak at $E \sim +750\,mV$ (E is given vs. $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)$). The voltammograms for the $Ag(TACT)^{2+}$ complex exhibit the same character as those for $Ag(TACP)^{2+}$ with a peak of metallic silver oxidation without its prior reduction. However, the observed redox system

$$Ag(TACT)^{2+} + e \rightleftarrows Ag(TACT)^+ \qquad (II)$$
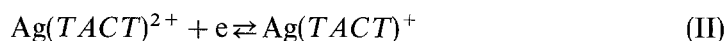
is irreversible in contrast to system (I) ($E_a \sim +160\,mV$, $E_c \sim -220\,mV$ at $v = 50\,mV/s$). It holds down to $v = 10\,mV/s$ ($\Delta E_{pac} \sim 300\,mV$); hence, we may only estimate the value of E_f^0 ($< +270\,mV$ vs. SHE).
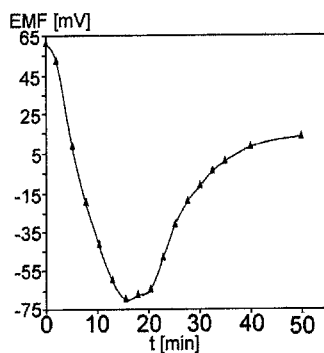
EMF [mV]

Fig. 3. Amperostatic reduction curve of $1 \times 10^{-3} M$ Ag($TACT$(ClO$_4$)$_2$) solution in $DMSO$; ($i = 1$ mA, EMF $vs.$ Ag^0|0.01 M AgClO$_4$ ($DMSO$) + 0.1 M (C$_2$H$_5$)$_4$NClO$_4$ ($DMSO$), $\mu = 0.1$ ((C$_2$H$_5$)$_4$NClO$_4$), $T = 298$ K

The amperostatic reduction of $1 \times 10^{-3} M$ AgL(ClO$_4$)$_2$ solutions (previously additionally oxidized at maximum EMF, $i = 1$ mA) was carried out for $L = TACP$ and $TACT$. The obtained curves differed considerably from the typical ones of this type, indicating two potential drops for Ag(II)/Ag(I) and Ag(I)/Ag(O) systems. The relation EMF $= f(t) = f(Q)$ showed the potential minimum and increase of EMF value of the systems with advancing reduction processes. The same phenomenon was observed for these complexes in water and PC [4-6], and we can conclude that we deal (similarly as in H$_2$O and PC) with a reduction of the AgL^{2+} complex in the descending part of the coulometric curves and with the oxidation of metallic silver resulting from a disproportionation of AgL^+ in the ascending one. A typical amperostatic reduction curve for a Ag($TACT$(ClO$_4$)$_2$) solution is shown in Fig. 3.

Examination of the Ag(II)/Ag(I)-TMTACT system

In contrarst to Ag($TACT$)$^+$ and Ag($TACP$)$^+$, the Ag($TMTACT$)$^+$ complex does not disproportionate in $DMSO$. We attempted a synthesis of Ag($TMTACT$)$^{2+}$ by oxidation of the Ag(I) compound. Neither oxidation of a $2 \times 10^{-3} M$ solution of Ag($TMTACT$)$^+$ under potentiostatic (E $= +300$ mV $vs.$ Ag^0|0.01 M AgClO$_4$ ($DMSO$) + 0.1 M (C$_2$H$_5$)$_4$NClO$_4$ ($DMSO$) electrode) nor under amperostatic conditions ($i = 1$ mA) afforded the desired product. In both cases, the oxidized solutions turned brown. The absorption maximum was observed at 688 nm, whereas the peak at 402 nm (characteristic for Ag($TMTACT$)$^{2+}$) was absent. Moreover, we did not observe any increase of the potential under amperostatic conditions which would indicate the formation of a Ag(II) complex. Regardless of the conditions, the absorption at $\lambda = 688$ nm increased steadily as the oxidation proceeded. The oxidation of a $2 \times 10^{-3} M$ solution of the ligand under the same conditions did not cause any change in colour.

The failure of our attemps of an electrochemical synthesis of Ag($TMTACT$)$^{2+}$ became understandable after CVA investigations. The following CVA curves were recorded: 1) $2 \times 10^{-3} M$ solution of ligand, 2) $2 \times 10^{-3} M$ solution of Ag($TMTACT$(ClO$_4$)) and 3) $2 \times 10^{-3} M$ solution of Ag($TMTACT$(ClO$_4$)$_2$) synthesized in water and transferred to $DMSO$. Similar to other solvents [5-7], $TMTACT$ easily oxidizes in $DMSO$. Its oxidation starts at $E \geqslant +200$ mV, and on the voltammograms we can observe two anodic peaks ($E_1 \sim +350$ mV,
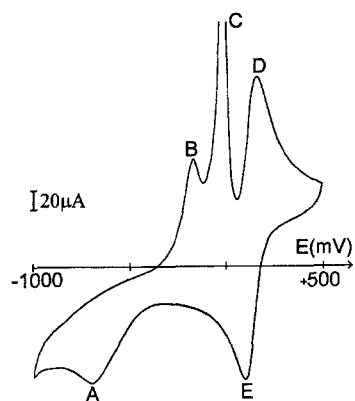
Fig. 4. CVA curve of $2 \times 10^{-3} M$ $Ag(TMTACT(ClO_4))$ solution in $DMSO$; $v = 50\,mV/s$, E $vs.$ $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO) + 0.1\,M$ $(C_2H_5)_4NClO_4$ $(DMSO)$, $\mu = 0.1$ $((C_2H_5)_4NClO_4)$, $T = 298\,K$

$E_2 \sim +750\,mV)$ without their cathodic counterparts. As with the other ligands, after several cycles the electrode was coated by an insoluble oxidation product. The voltammogram of a $2 \times 10^{-3} M$ $Ag(TMTACT(ClO_4))$ solution (Fig. 4) shows a peak in the cathodic region (A) connected with the reduction of $Ag(TMTACT)^+$ to metallic silver, Ag^0 oxidizes in the anodic part of the CVA curve to the Ag(I) complex (peak B) and to Ag^+ ions (a big desorption peak C at $E \sim O\,mV$). As a result of the high stability of the complex, the redox system $Ag(TMTACT)^+ + e \rightleftarrows Ag^0 + TMTACT$ is irreversible ($\log \beta = 7.84$). This curve clearly confirms the system

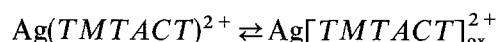$$Ag(TMTACT)^{2+} + e \rightleftarrows Ag(TMTCT)^+ \qquad (III)$$

with a pair of peaks (D and E) whose ΔE_{pac} of about $70\,mV$ at $v = 50\,mV/s$ indicates its reversibility. The value of formal potential for system (III) determined in 5 measurements amounts to $E_f^0 = +130 \pm 3\,mV$ $vs.$ $Ag^0|0.01\,M$ $AgClO_4$ $(DMSO)$ $+ 0.1\,M$ $(C_2H_5)NClO_4$ $(DMSO)$ $(+400\,mV$ $vs.$ SHE).

The voltammograms of solutions 2) and 3) in the potential region excluding the reduction of $Ag(TMTACT)^+$ ($E = -300$ to $+500\,mV$) did not give evidence of the metallic silver oxidation peaks B and C, thus indicating the absence of a disproportionation process. Moreover, in contrast to $Ag(TACT)^{2+/+}$ and $Ag(T\,ACP)^{2+/+}$ systems, the value of formal potential of the $Ag(T\,MT\,ACT)^{2+/+}$ system is higher than the potential of the $Ag^0 - e \rightarrow Ag^+$ process. This formally accounts for the disproportionation process of Ag(I) complexes with $TACT$ and $TACP$ and its absence in the case of $Ag(TMTACT)^+$.

The formal potential of system (III) ($E_f^0 = +130\,mV$) and the oxidation potential of $Ag(TMTACT)^+$ are close to the potential of the ligand solution oxidation ($E \geqslant 200\,mV$). Therefore, during the oxidation of $Ag(TMTACT)^+$ solution and after the transfer of $Ag(TMTACT)^{2+}$ synthesized in water to $DMSO$, the following processes take place.:

$$Ag(TMTACT)^{2+} + TMTACT \rightleftarrows Ag(TMTACT)^+ + [TMTACT]_{ox}^+$$
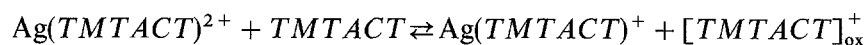
or internal transfer of an electron:

$$Ag(TMTACT)^{2+} \rightleftarrows Ag[TMTACT]_{ox}^{2+}$$

where "ox" denotes an unidentified oxidized form of the ligand. This explains why all our attempts of the synthesis of Ag(II) complex with this ligand in $DMSO$ failed and why the value of molar absorptivity ($\varepsilon = 710$ for Ag($TMTACT$)$^{2+}$ at λ_{max}, Table 1) is certainly far too small.

The obtained values of K_d indicate that the disproportionation of the Ag(I)-tetraazamacrocycle complexes in $DMSO$ occurs to a lower extent than in water or propylene carbonate. This is so, because $DMSO$, contrary to H_2O and PC, is a solvent with a high donor number ($DN = 29.8$) and with a soft donor center on the sulfur atom, stabilizing the lower oxidation number of ions. However, as opposed to AN, in which the disproportionation process does not occur, it has a hard donor center on the oxygen atom. Hence, $DMSO$ is able to stabilize Ag(II). Therefore, for the appropriate structure of the macrocyclic ligands and of AgL^+ and AgL^{2+}, the disproportionation becomes possible in $DMSO$; yet it does not occur in the case of Ag($TMTACT$)$^+$.

Moreover, the formal potential of the Ag(II)/Ag(I) system is highest in the presence of $TMTACT$ in all solvents under investigation [4–7], and the values of the disproportionation constants in H_2O and PC are the smallest. Considerably smaller stabilization of Ag^{2+} ions results in this case from the $TMTACT$ structure and from coordination of the metal ion in the square pyramide symmetry [11, 12]. The average distance of the metal ion from the N_4 plane ranges from 0.2 to 0.5 Å, which leads to an increase of the length of Me–N bond and a greater stability of the complexes with the lower oxidation number of the metal. Moreover, the exposure of Ag$^+$ and Ag^{2+} ions in the complexes with this ligand increases the possibility of their solvation and highly influences the stability of Ag(I) and Ag(II) complexes to the solvent.

In the case of a solvent with only one soft donor center (acetonitrile), the stabilization of Ag($TMTACT$)$^+$ is so significant that the formal potential of the Ag($TMTACT$)$^{2+/+}$ system is higher by about 500 mV than those of the other systems. The possibility of interactions between a hard acid (Ag^{2+}) and a hard donor center (oxygen atom in $DMSO$) decreases the difference between the values of the formal potential of the systems under investigation.

The disproportionation constant values and the established $E_{f\,AgL/AgL}^{0\,2+\,/+}$ values indicate the greater stability of Ag($TACP$)$^{2+}$ regardless of the solvent used [4, 6, 7]. It is also confirmed by the values of the bonding energy of the 3d electrons in Ag(II) complexes with the macrocycles under study, established by means of the ESCA method, with a maximum for the 15-membered ring [13]. These facts can be explained if a square planar structure of the complexes is assumed and the relationship between the bonding cavity diameter and the optimized lengths of the Me–N in the dependence of the macrocycle size is considered.

The *Busch* [14] and *Hancock* [15] calculations show that, in the best case, the metal ion forms bonds which are by 0.1–0.2 Å shorter than the macrocycle diameter.

The length of the Ag–N bond for the Ag(II) complexes with the square planar structure is 2.16 ± 0.03 Å [16, 17], and the diameters of the bonding cavity in $TACT$ and $TACP$ are 2.05–2.07 Å and 2.23–2.28 Å, respectively [15, 18]. Hence, one can assume that the most favourable ligand for the stabilization of Ag^{2+} is tetraazacyclopentadecane, which is in good agreement with the results presented above.

Experimental

Tetraazacyclic amines were used as purchased (Aldrich). The ligand solutions were standarized by pH-metric titration with standard $HClO_4$ in water-$DMSO$ (10:1 v/v) solutions. $(C_2H_5)_4NClO_4$ was synthesized according to the procedure given by *Kolthoff* and *Thomas* [8]. $DMSO$ (Merck) was initially fractionally frozen, kept over 4 Å molecular sieves, and distilled over CaH_2 under reduced pressure after 3 days. The water content was verified chromatographically. Solutions of $AgClO_4$ in $DMSO$ were prepared by dissolving weighed ammounts of compound in freshly distilled $DMSO$.

Acknowledgements

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