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Two new silver(I) complexes with 2,4,6-tris(2-pyridyl)-1,3,5-triazine (*tptz*): Preparation, characterization, crystal structure and alcohol oxidation activity in the presence of oxone

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ABSTRACT

Two new silver(I) complexes ((tptz)Ag₂(NO₃)₂ and [Ag₅(tptz)₄](NO₃)₅) with 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) have been synthesized and characterized by X-ray diffraction, elemental analysis, ¹H NMR, IR, fluorescence, UV–Vis spectroscopy and electrochemistry. Oxidation of alcohols to their corresponding aldehydes and ketones was conducted with one of the Ag complexes as a catalyst, soluble enough in organic solvent, using oxone (2KHSO₅·KHSO₄·K₂SO₄) as an oxidant under biphasic reaction conditions (CH₂Cl₂/H₂O) and tetra-*n*-butylammonium bromide as phase transfer agent under air at room temperature.

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1. Introduction

A combination of conjugated ligands and electron-rich metal centers can produce low energy electronic interactions between metal centers and ligands, resulting in a product with interesting optical or electronic properties. Complexes of silver(I) and N-heterocyclic ligands lead to the formation of a variety of geometric configurations and photophysical properties [1]. In recent years, 2,4,6-tris(2-pyridyl)-1,3,5-triazine (*tptz*), which functions simultaneously as a tridentate and a bidentate ligand, has gained considerable interest, because of its use as a spacer for designing supramolecular complexes [2].

The reactions of *tptz* and silver(I) nitrate at ratio of 1:2 in acetonitrile/water at many different ratios produce two different compounds together. We could separate each compound by optimizing the reaction conditions. In a mixture of acetonitrile/water at ratio of 9:1, **1** (*catena*-{[nitrato- μ_3 -2,4,6-tris(2-pyridyl)-1,3,5-triazinesilver(I)][(dinitrato- μ_2 -2,4,6-tris(2-pyridyl)-1,3,5-triazinesilver(I)]}) was formed and at the solvent ratio of 1:9, **2** (tetrakis($\mu_2, \mu_2, \mu_1: \mu_2, \mu_2, \mu_1: \mu_1, \mu_1: \mu_1, \mu_1-2, 4,6-tris(2-pyridyl)-1,3,5-triazine)$ pentasilver(I) nitrate hydrate (1/7)) was formed. At other ratiosboth compounds are formed together (see Section 4 for details). Both title compounds are silver(I) complexes of tptz, containing nitrate anions, which form part of the silver(I) atoms coordination sphere only in case of **1** and in case of **2** part of the nitrate anions is disordered. Moreover, 2 contains also water molecules of solvation, part of which is disordered. There are twelve *tptz* complexes of silver(I) deposited in the CCDC database [3–6]. Seven of these compounds also contain phosphine ligands [3,6], one is a mixed silver(I)-ruthenium(II) complex (reported as a new DNA cleavage agent) [4] and one contains also trifluoroacetate ligands bonded to silver(I) atoms [5]. The possibility of obtaining 1 along with 2 from one system corresponds to the reported observation, according to which it could be expected, that the product composition may be not related to the molar ratio of reactants [3]. It is speculated, that in these self-assembly processes the anion- π non-covalent interactions play a crucial role [5]. In the here reported particular case the presence of water in the used solvents seems to be an important factor to be considered as affecting the selfassembly processes route.

Some silver-based catalysts including electrolytic silver and supported silver catalysts, have been recently demonstrated for the selective oxidation of alcohols [7] but there are no reported surveys on the use of silver(1) complexes as homogenous catalysts in the alcohol oxidation reaction. The alcohol oxidation activity of **1** in the presence of oxone is considered with regard to the sufficient solubility of **1** in CH_2Cl_2 . The results have shown that the complex **1** is an efficient catalyst for the oxidation of primary and secondary alcohols. Although it is difficult to stop the oxidation of primary

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alcohols at the intermediate aldehyde stage, this system is very useful in the transformation of primary alcohols into aldehydes without over-oxidation to carboxylic acids (Table 2).

2. Results and discussion

The results of catalytic studies (see Section 4) have shown that the complex **1** (*catena*-{[nitrato-µ₃-2,4,6-tris(2-pyridyl)-1,3,5-triazinesilver(I)][(dinitrato-µ₂-2,4,6-tris(2-pyridyl)-1,3,5-triazinesilver(I)]}) is an efficient catalyst for the oxidation of primary and secondary alcohols. Although it is difficult to stop the oxidation of primary alcohols at the intermediate aldehyde stage, this system is very useful in the transformation of primary alcohols into aldehydes without over-oxidation to carboxylic acids (see Table 2, entries 1–4). Benzyl alcohols were oxidized to give the corresponding aldehvdes with a 100% conversion yield (Table 2, entries 1-4). The substrates bearing electron-donating and -withdrawing substituents bonded to the aromatic ring were compatible with this protocol. The change of nature of substituents (methyl, methoxy, and nitro) in the aromatic ring of benzyl alcohol to probe electronic effects displayed no regular trends in the conversion. With the exception of 1-indenol (Table 2, entry 8), aliphatic alcohols and secondary alcohols were less reactive in comparison to aromatic alcohols (Table 2, entries 5-10).

Both title complexes have been characterized by a number of different techniques, both in solid state and in solution.

Electronic spectra of **1** in acetonitrile/water (9/1) and of **2** in water/acetonitrile (9/1) solution were recorded and are very similar (Fig. 4S). The electronic spectra display two strong absorption bands at about ~205 and ~250 nm. These are clearly charge transfer in origin and the absorption band observed at ~290 nm can be assigned to the charge transfer from the coordinated ligand to the Ag(I) centre [8].

The IR spectrum recorded for **2** shows a broad band at ~3200– 3500 cm⁻¹ related to lattice water (antisymmetric and symmetric O–H stretching) and at ~1630 cm⁻¹ assigned to H–O–H bending mode) [9]. Peaks revealing the presence of the *tptz* ligand in the complex occur in the ranges 3100–2900 cm⁻¹ (aromatic C–H stretching vibrations), 1600–1550 cm⁻¹ [ν (C=N) and ν (C=C) stretches], 1470–1020 cm⁻¹ [ν (C–C) + ν (C–N) vibrations], and 810–710 cm⁻¹ (aromatic C–H deformation vibrations) [9]. The asymmetric stretch of the nitrate ion is split into a high-frequency N–O asymmetric stretch and to a lower-frequency symmetric stretch upon coordination. These occur at 1480 and 1250 cm⁻¹, respectively, for **1**. The appearance of a broad band at 1380– 1390 cm⁻¹ on the spectrum recorded for **2** is indicative of the presence of uncoordinated nitrate ions [10].

Fluorescence emission spectra of complex **1** or **2** in DMSO (Fig. 3S) are similar. The peaks at around 543.97 nm may be attributed to the intraligand emission ($\pi \rightarrow \pi^*$) from the *tptz* ligand. The fluorescence intensity for the complex **1** and **2** is larger than that for the free *tptz* ligand, probably due to the rigidity of the coordinated ligand in the complex in comparison to the free ligand. On the other hand, the fluorescence intensity enhancement may be due to the coordination of the free ligand to Ag(I) centre, reducing the non-radiative decay of the intraligand excited state.

Ag(II) ion in water is obtained from oxidation of $AgNO_3$ by strong oxidizing agents but it is unstable due to its powerful oxidizing nature in solution (standard redox potential: 1.98 V) and must be stabilized by coordination with organic ligands, most notably the nitrogen-containing heterocycles [1]. To test of the stabilizing effect of *tptz*, electrochemical studies were performed. From the electrochemical studies carried out for **1** (see Section 4 and Fig. 5S) it is concluded that the three ligand reduction pair peaks appear in the negative potential region of voltammogram, similarly to the previous results for the corresponding complexes of *tptz* with Ni and Fe [10]. The midpoint potential values for these peaks are: -0.15, -0.81 and -1.58 V, respectively. Also, an irreversible anodic wave is observed at around +0.5 V versus reference electrode, which is attributed to the oxidation of silver ion in the complex. It should be mentioned that the ligand has no redox peak in the positive potential region of the voltammogram.

The X-ray studies (Table 1) reveal, that in solid state in 1 there are two symmetry-independent silver(I) atoms (Fig. 1a). Ag1 atom is coordinated to pyridyl N12 and N13 atoms and to the triazine N11 atom from the *tptz* ligand, as well as to the nitrate O15 atom (Table 1S). Also a weaker bond to O25 atom from the same nitrate anion could be distinguished (Table 1S). Thus the coordination number of Ag1 atom could be given as 4 or 5. All ligands bonded to Ag1 atom lie in one plane. In order to provide a quantitative description of the coordination sphere also computations with the use of SHAPE software [11.12] were carried out. Five possible geometries were considered and the best fit was observed for PP-5 pentagon geometry [11] (the calculated figure of merit was 2.25 for this geometry; for ideal fit zero value is obtained; in this case the four remaining geometries yielded the analogous values at about 30). If the weaker Ag1-O25 bond is disregarded, the geometry of Ag1 atom coordination sphere could be described as square-planar. The square-planar geometry around Ag(I) atom is not unprecedented and there are well-characterized examples as recently reviewed by Young & Hanton [13].

Silver(I) coordination number three and unusual in silver(I) chemistry coordination number four seem to be characteristic for silver(I) *tptz* complexes [3–6], along with severely distorted coordination polyhedra [4]. Similarly, in case of Ag2 atom the closest coordination sphere consists of four atoms (pyridyl N14 atom and triazine N31 atom from the *tptz* ligand, as well as O16, O36^{*i*}

Table 1Selected X-ray data for complex 1 and 2.

	1	2
Formula	(C ₁₈ H ₁₂ N ₆)Ag ₂ (NO ₃) ₂	[Ag ₅ (C ₁₈ H ₁₂ N ₆) ₄](NO ₃) ₅ (H ₂ O) ₇
Formula weight	652.10	2224.86
Temperature (K)	120(2)	100(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	Pnna
a (Å)	14.969(4)	24.384(5)
b (Å)	6.593(3)	28.832(6)
c (Å)	20.767(4)	11.083(4)
β (°)	108.42(3)	
V (Å ³)	1944(2)	7792(4)
Z, $ ho_{ m calc}$ (g cm $^{-3}$)	4, 2.227	4, 1.897
μ (mm $^{-1}$)	2.08	1.33
$F(0\ 0\ 0)$	1272	4432
Crystal size (mm)	$0.14 \times 0.06 \times 0.05$	$0.14 \times 0.11 \times 0.06$
θ Range (°)	4.7-38.6	4.2-35.0
Reflections: total/ unique	19592/10118	80161/17127
R _{int}	0.059	0.053
Absorption corrections	analytical	analytical
Minimum, maximum transmission factors	0.796, 0.908	0.832, 0.933
Data/restraints/ parameters	10118/0/307	17127/0/645
Goodness-of-fit (GOF) on F ²	0.683	1.04
$R_1 \left[I > 2\sigma(I) \right]$	0.036	0.035
wR_2 (all data)	0.042	0.036
Maximum,	1.55, -0.98	2.00, -1.01
minimum $\Delta ho_{ m elect}$ (e Å ⁻³)		



Fig. 1. Atom labeling scheme for the symmetry-independent part in complex **1** (a) and complex **2** (b). Only the closest coordination sphere (see text) of the Ag(I) atoms is indicated (with open lines). For complex **2** (b) the nitrate anions and water molecules are omitted. Symmetry codes: [i] 2 - x, y - 0.5, -z + 0.5, [ii] x, 0.5 - y, 1.5 - z.

atoms from two nitrate anions, Table 1S). These atoms lie in vertices of a very distorted tetrahedron. Also weaker bonds to O26^{*i*} and O26 atoms from the same nitrate anions participating in Ag2 closest coordination sphere could be distinguished. Thus geometry of the whole coordination sphere of Ag2 atom is very irregular (Table 1S). The analogous calculations as for Ag1 atom with the use of SHAPE software [11,12], taking into consideration fitting to five ideal polyhedra, yield the following figures of merit: 24.39 for hexagon

HP-6, 12.26 for pentagonal pyramid PPY-6, 18.58 for octahedron OC-6, 13.18 for trigonal prism TPR-6, 14.01 for Johnson pentagonal pyramid JPPY-57. In Table 2S the interplanar angles between planes of the ligands for Ag1 and for Ag2 central atoms, as well as deviations of the central atoms from the ligands planes are given.

The *tptz* ligand is generally considered as a rigid ligand with an extended π system [3]. Both coplanar, as well as nearly coplanar

(with one pyridyl ring twisted with respect to the remaining molecule part) forms of this ligand have been reported for silver(I) complexes [3]. In the *tptz* ligand in **1** the rings with N11 atom, with N12 atom and with N13, respectively, are almost coplanar; the ring with N14 atom is bent with respect to the plane of these rings (see Table 2S for the corresponding interplanar angles). The *tptz* ligand bonding mode could be described as μ_3 - μ_2 linking together Ag(I) centres [3].

Thus defined units (comprising two *tptz* ligands, four silver(I) atoms and five nitrate anions) are repeated along [0 1 0] direction to form a one-dimensional coordination polymeric structure (Fig. 2a). The neighbouring units are linked by nitrate O36 atom, which further coordinates to Ag2 atom at [iv] 2 - x, 0.5 + y, 0.5 - z.

The adjacent polymeric chains (see Article text) are interconnected *via* the following stacking interactions involving *tptz* ligands rings (in brackets the range of the shifts of atoms of one ring with respect to the plane of the interacting ring is given): ring with N13 atom and ring with N12 atom at 1 - x, 0.5 + y, 0.5 - z

(3.147(4) - 3.472(5) Å), ring with N13 atom and ring with N12 atom at 1 - x, y = 0.5, 0.5 - z (3.060(5)=3.384(5) Å), ring with N14 atom and ring with N14 atom at 2 - x, 2 - y, 1 - z (3.208(4)-3.220(4)Å), ring with N14 atom and ring with N14 atom at 2 - x, 1 - y, 1 - z(3.039(4)–3.050(5) Å). Another kind of interaction involves the ring with N11 atom and the nitrate anion with N15 atom at 1 - x, 0.5 + y, 0.5 - z (anion atoms are shifted from the interacting ring plane at 3.240(4)–3.342(4) Å), as well as the ring with N11 atom and the nitrate anion with N15 atom at 1 - x, y = 0.5, 0.5 - z (anion atoms are shifted from the interacting ring plane at 3.203(4)-3.305(4) Å). This kind of π ...anion interaction has been considered by Zhou et al. for *tptz* ligands interacting with ClO₄⁻, BF₄⁻ or PF₆⁻ anions as a directing factor in formation of Ag(I) coordination networks [2]. In **1** numerous weak hydrogen bonds of C-H···O type and also C-H···N(triazine ring from *tptz* ligand) (Table 3S) could be distinguished.

In **2** there are four symmetry-independent silver(I) atoms (Fig. 1Sb). Ag1 atom is bonded to four atoms from two *tptz* ligands:



Fig. 2. Formation of a one-dimensional polymeric structure in complex **1** (a) and a cationic unit in complex **2** (b). Symmetry codes: [ii] x, 0.5 - y, 1.5 - z; [iii] x, y - 1, z; [iv] 2 - x, 0.5 + y, 0.5 - z. In (a) the unit repeating along [0 1 0] (see text) is marked in black. Selected atoms are labeled. The continuation of the polymeric structure is denoted with black dashed lines. In (b) the symmetry-independent part is marked in black.

triazine N111 and N111^{*ii*} atoms, pyridyl N131 and N131^{*ii*} atoms. These N atoms are of very distorted tetrahedral arrangement. This distortion creates another possible coordination site, which is occupied by O25 and O25ⁱⁱ atoms from two weakly monocoordinated nitrate anions. Thus, taking into account all these ligands, the coordination environment of Ag1 is very irregular and could be described as an extremely distorted octahedron (the calculations with the use of SHAPE software [11,12] lead to the following figures of merit: 16.35 for hexagon HP-6, 19.25 for pentagonal pyramid PPY-6, 10.20 for octahedron OC-6, 15.17 for trigonal prism TPR-6, 20.37 for Johnson pentagonal pyramid JPPY-5). Similar motifs in silver(I) coordination chemistry have already been observed and are generally interpreted as semi-coordination of the silver(I) atoms by nitrate anions [12]. Ag2 closest coordination sphere comprises triazine N211, N212 atoms and pyridyl N122, N141 atoms, forming a distorted octahedron. Also weak coordination of nitrate 016 and 015ⁱⁱⁱ atoms could be distinguished, which, if not neglected, leads to the conclusion, that Ag2 coordination sphere is very distorted octahedral, but not as extremely distorted as in case of Ag1. The strongest coordination bonds to Ag3 atom are those involving N atoms from two *tptz* ligands: pyridyl N142^{*ii*}, N142, N121^{*ii*}, N121 atoms. These atoms lie in vertices of a distorted tetrahedron. Also a weaker coordination to other N atoms from the two *tptz* ligands is observed: triazine N121^{*ii*}, N211, N211^{*ii*}, N212 atoms, also of distorted tetrahedral arrangement. When the two tetrahedral, consisting of tptz N atoms, are taken together and the possible coordination geometries are fitted with SHAPE software the lowest figure of merit at 3.56 is obtained for dodecahedron DD-8 geometry (also small values are obtained for square antiprism SAPHR-8: 4.30; Johnson – biaugmented trigonal prism JBTP-8: 4.56). The coordination environment of Ag4 atom is very similar as in case of Ag1 atom. The closest coordinated atoms are N atoms from two tptz ligands: triazine N312ⁱⁱ, N312 atoms (two longer Ag-N bonds) and pyridyl N132, N132ⁱⁱ atoms (two shorter Ag-N bonds), forming a distorted tetrahedron. The specific distortion of this tetrahedron makes it possible for weak monodentate coordination of two nitrate anions (through $O26^{iii}$ and $O26^{iv}$ atoms. respectively) to occur and the resulting coordination sphere is very distorted octahedral.

Characteristic pentameric units are formed in **2**, comprising four *tptz* ligands (two symmetry-independent ligand molecules and the two symmetry-related ligand molecules at [ii] x, 0.5 - y, 1.5 - z) interconnected by five silver(I) atoms (four symmetryindependent Ag1, Ag2, Ag3 and Ag4 atoms and the symmetry-related Ag2 atom at [ii] x, 0.5 - y, 1.5 - z; Fig. 2b). The shortest Ag. Ag3 of 3.496(2) Å). The formation of such units is connected with considerable distortion of the *tptz* ligands and their unusual conformation (see description of *tptz* ligand for **1**), as illustrated by the interplanar angles between the planes of the rings constituting these ligands, listed in Table 3S. The pentameric units are arranged in layers parallel to (1 0 1). Between the layers spaces are formed, which contain disordered nitrate anions and water molecules, as well as the ordered water molecules.

In **2** water molecules participate as donors in O–H···O hydrogen bonds, in which other water molecules or nitrate anions act as acceptors (Table 4S). Also numerous weak hydrogen bonds of C– H···O type, along with C–H···N (triazine ring from *tptz* ligand), could be found (Table 5S). The ordered nitrate anions are distributed within the layers of complex units participating in the contacts described above. Also numerous stacking interactions between rings constituting *tptz* ligands are observed, the majority within the mentioned pentameric units (the following contacts of this kind are observed, with the range of the shifts of atoms of one ring with respect to the plane of the interacting ring, respectively: ring with N112 atom and ring with N142 atom at *x*, 0.5 - y, 1.5 - z, 3.191(1)-3.664(4) Å; ring with N142 atom and ring with N141 atom, 3.273(3)-3.466(5) Å; ring with N112 atom and ring with N142 atom at *x*, 0.5 - y, 1.5 - z, 3.191(3)-3.664(4) Å; ring with N122 atom and ring with N121 atom, 3.205(4)-3.391(3) Å; ring with N121 atom and ring with N111 atom at *x*, 0.5 - y, 1.5 - z, 2.969(4)-3.358(3) Å), but also between the adjacent units (ring with N141 atom and ring with N122 atom at *x*, 0.5 - y, 0.5 - z, the shifts of atoms of one ring with respect to the plane of the interacting ring are in the 3.265(3)-3.398(4) Å range). When also weaker coordination of nitrate anions to the Ag(I) atom is taken into account, it could be noted, that the pentameric units are linked by these anions to form interlinked layers perpendicular to [0 1 0].

In general, both in **1** and **2** a preference towards very distorted tetrahedral geometry of Ag(I) centres closest coordination sphere could be observed. However, as the distortion is extreme, hardly available new coordination sites are created, making it possible for weaker bonds to other ligands to occur, as Ag(I) is a d¹⁰ system with no significant stereochemical preferences [13]. However, also an important factor determining this coordination mode is some degree of rigidity within the *tptz* ligand itself.

It is suggested that a structure in the solid-state is preserved in solution, which may be likely to hold for most solvents with low polarity. However, for polar solvents, such as water, able to promote ligand exchange, significant structural modifications may occur, which would drastically change the structure of the complex in solid state, while promoting equilibria with other species stabilized by solvation [14–23]. ¹H NMR and ¹³C NMR spectra recorded for **1** in Me₂SO-d₆ were investigated. ¹H NMR and ¹³C NMR spectra suggest that the ligand unit is dissociated in solution. ¹H NMR, ¹³C NMR, COSY and HSQC spectra of the complex are consistent with that of the ligand itself in solution. Four ¹H NMR peaks in the range of 7.9–9 ppm and six ¹³C NMR peaks in the range of 125–170 ppm clearly signify that all *tptz* ligands are released. Such a fact indicates that the Ag–N bonds are labile in solution, which is also reported by others [24–26].

3. Conclusions

Two different silver(I) complexes were isolated in the reaction of *tptz* ligand with silver(I) nitrate. The complexes differ in structure: **1** comprises polymeric chains of $[(C_{18}H_{12}N_6)_2Ag_4(NO_3)_4]$ units, in **2** pentameric $[Ag_5(C_{18}H_{12}N_6)_4](NO_3)_5(H_2O)_7$ units are present. It has been shown, that complex **1** exhibits catalytic properties in oxidation of alcohols. This study involves not only presentation of a new catalytic system, but also may be useful in design of new catalysts.

4. Experimental

4.1. Syntheses

Complex **1** ((*tptz*)Ag₂(NO₃)₂) was synthesized by adding of 2,4,6-tris(2-pyridyl)-1,3,5-triazine (*tptz*) (1 mmol, 0.312 g) to a solution of silver nitrate (2 mmol, 0.34 g) in 20 ml of acetonitrile/ water (9/1). The mixture was stirred for about 1 h at room temperature. The resulting yellow precipitate was filtered off and recrystallized by using acetonitrile/water (9/1) to give yellow crystals. After 4 days, yellow crystals of **1** were obtained that were suitable for X-ray determination. *Anal.* Calc.: C, 33.15; H, 1.85; N, 17.18. Found: C, 33.54; H, 1.97; N, 17.41%. ¹H NMR for *tptz* in CDCl₃ (ppm): 8.99 (d, 1H), 8.88 (d, 1H), 7.99 (t, 1H), 7.57 (t, 1H). ¹³C NMR in CDCl₃ (ppm): 172.10 (C1), 152.98 (C2), 150.41 (C3), 137.13 (C4), 126.56 (C5), 125.15 (C6). ¹H NMR for **1** in DMSO (ppm): 8.95 (d, 1H), 8.78 (d, 1H), 8.2 (t, 1H), 7.82 (t, 1H).

Complex **2** ($[Ag_5(tptz)_4](NO_3)_5 \cdot 7H_2O$) was synthesized by adding of 2,4,6-tris(2-pyridyl)-1,3,5-triazine (*tptz*) in 2 mL of warm acetonitrile (1 mmol, 0.312 g) to a solution of silver nitrate (2 mmol, 0.34 g) in 10 mL of water. The mixture was stirred for about 10 h at 313 K in the dark. The resulting yellow precipitate was filtered off and recrystallized by using water/acetonitrile (9/ 1) to give yellow crystals. After 10 days, orange crystals of **2** were obtained that were suitable for X-ray determination. *Anal.* Calc.: C, 38.87; H, 2.81; N, 18.26. Found: C, 38.03; H, 2.61; N, 18.01%. ¹H NMR for **2** in DMSO (ppm): 8.83 (d, 1H), 8.50 (d, 1H), 8.08(t, 1H), 7.64 (t, 1H).

4.2. IR spectra

IR spectra (4000–400 cm⁻¹ wavenumber range) were measured on a FT-IR JASCO 460 spectrophotometer as KBr pellets.

4.3. Fluorescence emission spectra

Fluorescence emission spectra for solutions of **1** and **2** in DMSO were recorded with excitation wavelength of 200 nm at room temperature on Cary Eclipse Fluorescence spectrophotometer equipped with quartz cuvettes of 1 cm path length. The representative fluorescence emission spectrum is depicted in Fig. 3S.

4.4. UV-Vis spectra

Electronic spectra of **1** in acetonitrile/water (9/1) and of **2** in water/acetonitrile (9/1) solution were recorded (Fig. 4S) on a Cary 100 Bio Varian UV–Vis spectrometer.

4.5. Catalytic reaction

Based on the observed results from optimization of the reaction conditions, the catalyst, tetra-*n*-butylammonium bromide, substrate and oxone were used in the following molar ratio: 1:10:50.50. Reactions were performed at room temperature under air in a (1:5) mixture of CH_2CI_2/H_2O .

After optimization, the oxidations of wide variety of primary and secondary aliphatic and benzylic alcohols to corresponding aldehydes or ketones were investigated and the details of catalytic activity with respect to oxidation of alcohols are recorded in Table 2.

4.6. Electrochemistry

Electrochemical studies were carried out in a conventional three electrode cell using Pt electrode as a counter electrode and Ag wire quasi-reference electrode, and a 2 mm diameter glassy carbon disk electrode as a working electrode. All potentials were reported versus Ag/AgCl reference electrode. Prior to all measurements the acetonitrile electrolyte was degassed at least for 10 min and throughout the measurement the cell was kept under nitrogen gas atmosphere to avoid oxygen interference. Electrochemical measurements were run using Zahner-Zennium potentiostat-galvanostat under ambient temperature.

Electrochemical studies for **1** in acetonitrile solvent containing 0.05 M of supporting electrolyte were carried out and a typical voltammogram is presented in Fig. 5S.

4.7. NMR spectra

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 MHz spectrometer, using CDCl₃ or DMSO as a solvent at 298.5 K.

Table 2

Oxidation of alcohols catalyzed by complex 1.

Entry	Substrate ^a	Conversion (%) ^b	TON ^c
1	СН2ОН	100	50
2	CH ₃	100	50
3	OMe	100	50
	СН2ОН		
4		100	50
5	CH ₂ OH	88	44
6	CH ₃	93	46.5
	ОН		
7	Н ₃ С-ОН	90	45
8	ОН	100	50
9	OH	73	36.5
10	OH	66	33
	$\Delta \Delta /$		

^a The molar ratios for catalyst: phase transfer agent: substrate: oxidant are 1:10:50:50, respectively. The reactions were run for 2 h at room temperature in a biphasic medium (CH_2CI_2/H_2O).

 $^{\rm b}\,$ The GC conversion (%) are measured relative to the starting alcohol after 2 h.

^c TON = (mmol of products)/mmol of catalyst.

4.8. X-ray studies

4.8.1. X-ray measurement

Both crystals of complex **1** and **2** were measured on Xcalibur PX diffractometer with Mo K α radiation (see Table 1S for selected X-ray data). The X-ray measurement for complex **1** was performed at 120 K and for complex **2** at 100 K.

4.9. Refinement

Both structures were solved by direct methods using SHELXS program and refined using SHELXL [27].

For complex **1** all H atoms were generated based on the known geometry and refined with $U_{eq} = 1.2U_{eq}$ (parent atom).

For complex 2 the atoms constituting the complex symmetryindependent part (2.5 silver(I) atoms, 2 ligand molecules), as well as two ordered nitrate anions lying in special positions on twofold axes, were easily found on the E-map. The remaining maxima were interpreted as arising due to the presence of two symmetry-independent water molecules (with O1W and O2W atoms, respectively) and a disordered nitrate anion, covering 1.5 of the positive charge. The disorder of the nitrate anion seems to be cooperative with disorder of water molecules occupying very near sites. The anion disorder was assumed to consist of three half-occupancy components (with N17, N18 and N19 atoms, respectively), essentially related by shifts along the *c* axis. The neighbouring components would be very near, with short $0 \cdots 0$ contacts, therefore they cannot occupy these sites in the crystal structure simultaneously. Each of the anion half-occupancy components seems to be cooperatively disordered with a half-occupancy water molecule (with O17W, O18W and O19W atoms, respectively) at a position very near to the anion N atom. The assumed model was first carefully refined with DFIX restraints setting the disordered anion components N–O bond lengths at 1.20(2) Å with isotropic temperature factors for the anion atoms, as well as the cooperatively disordered water molecules. Subsequently, the DFIX restraints were removed. Into thus refined model anisotropic temperature factors were introduced gradually to prevent the refined matrix from going singular. At this stage it was possible to find at the difference Fourier map positions of H atoms bonded to the ordered water molecule (O1W). The water molecule with O2W atom was refined as disordered in two positions (the refined occupancy factors of 0.60(3) and 0.40(3) for O2W and O3W component, respectively). It seems, that both disorder components share the same H atoms positions, which is confirmed by hydrogen bonding network and the possibility of their finding on the difference Fourier map. The H atoms bonded to water molecules were first refined with DFIX restraints (O–H bond length at 0.820(2) Å and U_{eq} = 1.5 U_{eq} (parent atom)) with O2W and O3W components coordinates constrained at the same time. Subsequently, AFIX 3 constraints were used to constrain the water H atoms parameters and constraints were removed from O2W and O3W components coordinates (it was necessary to use there constraints to prevent O2W/O3W components shifts changing the O-H bond lengths during the refinement). All remaining H atoms bonded to the ligand C atoms were generated from the known geometry. On the final difference Fourier map the highest peak of 1.55 $e/Å^3$ was present at 0.08 Å from the Ag2 atom. All ten highest peaks on the final difference Fourier map were located in the neighbourhood of Ag atoms.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.07.005.

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