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Synthesis, Crystal Structure, and Luminescence Properties of the Complex of Silver(I) Perrhenate with *N*-(2-Aminoethyl)piperazine

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Abstract—The reaction of $AgReO_4$ with *N*-(2-aminoethyl)piperazine, $C_6H_{15}N_3$ (L), gave a new compound $Ag(L)(ReO_4)$ (**I**). The crystals of **I** are monoclinic, space group $P2_1/c$, $a = 15.067(1)$ Å, $b = 11.616(1)$ Å, $c = 14.259(1)$ Å, $\beta = 108.40(1)°$, $V = 2368.0(3)$ Å^3, ρ(calcd.) = 2.734 g/cm^3, $Z = 8$. The structure of **I** consists of cationic polymeric chains $[Ag(L)]^+_\infty$ connected to the $[ReO_4]^-$ anions by the N–H···O hydrogen bonds to form a 3D supramolecular assembly. The Ag^+ ions have a T-shaped coordination with the ligand N atom functioning as a tridentate bridge between the silver atoms (CIF file CCDC no. 1034044). Compound **I** possesses fluorescence.

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INTRODUCTION

The metal-organic compounds of d^{10} metals with multidentate ligands can be regarded as precursors of organic-inorganic hybrid materials. The growing interest in these compounds is related to their unusual structures and the potential application as luminescent materials such as optical sensors, light emitting diodes (LED), etc. [1–3]. The preparation of these compounds is affected by many factors such as the coordination preference of the metal, geometric characteristics of organic ligands, the nature of counterions, the solvents used, and other. Among the ligands suitable for the synthesis of luminescent compounds, of interest is *N*-(2-aminoethyl)piperazine (L) containing three different nitrogen atoms: two piperazine ring nitrogens (N and NH) and one nitrogen of the NH_2 group. Therefore, L can act as both chelating and bridging ligand. In addition, L can participate in hydrogen bonding, thus forming supramolecular assemblies.

To date, two new coordination complexes of $HgCl_2$ with *N*-(2-aminoethyl)piperazine have been obtained and studied by X-ray diffraction: $[Hg^{II}(\mu_2\text{-}LH)Cl_2]_2[Hg^{II}_2(\mu_2\text{-}Cl)_2Cl_4] \cdot 2H_2O$ and $[Hg^{II}_4(\mu_3\text{-}L)_2(\mu_2\text{-}Cl)_2Cl_6]$ [3]. In one of these complexes, the ligand is monoprotonated and in the other complex, it is neutral. The former compound comprises two types of Hg(II) complexes: discrete mononuclear $[Hg^{II}(\mu_2\text{-}LH)Cl_2]^+$ and binuclear $[Hg^{II}_2(\mu_2\text{-}Cl)_2Cl_4]^-$. In addition, the structures of some coordination compounds of Cu, Zn, and Cd saccharinates $[M^{II}(L)_2(Sac)_2]$, where Sac is the saccharinate anion [4, 5], were determined. In the three above-indicated compounds, L behaves only as a chelating agent being attached to the metal atom via piperazine-ring and NH_2-group nitrogen atoms, thus forming a five-membered ring. No polymer formation was noted in the cited publications.

This work describes the preparation of the silver perrhenate complex $[Ag(L)(ReO_4)]$ (**I**) and study of its crystal structure and luminescence spectra.

EXPERIMENTAL

Silver perrhenate was prepared by the reaction of NH_4ReO_4 with $AgNO_3$ [6], while *N*-(2-aminoethyl)piperazine was a commercial (Aldrich) chemical.

Synthesis of I. Weighed portions of $AgReO_4$ (0.27 g, 0.64 mmol) and *N*-(2-aminoethyl)piperazine (0.08 g, 0.63 mmol) were separately dissolved in acetonitrile (4 mL), and the solutions were mixed. The observed turbidity of the solution was eliminated by dropwise addition of aqueous ammonia with stirring. The resulting solution was filtered and kept for 2 weeks in the dark for slow evaporation of the solvent. The prismatic light brown crystals that formed were separated from the solution, washed with a small amount of ethanol, and dried in air.

Table 1. Crystal data and X-ray experiment details for structure **I**

Parameter	Value
M	487.28
Color, habit	Colorless, block
Crystal size, mm	$0.15 \times 0.10 \times 0.08$
System; space group	Monoclinic; $P2_1/c$
Unit cell parameters:	
a, Å	15.067(1)
b, Å	11.616(1)
c, Å	14.259(1)
β, deg	108.40(1)
V, Å^3	2368.0(3)
Z	8
ρ(calcd.), g/cm^3	2.734
μ, mm^{-1}	11.867
F(000)	1808
Diffractometer	Enraf Nonius CAD4
T, K	293(2)
Radiation (λ, Å)	MoK_α (0.71073), graphite monochromator
Scan mode	ω
θ Range, deg	2.26–25.99
Ranges of indices	$-18 \le h \le 17$, $-14 \le k \le 14$, $-1 \le l \le 17$
Total number of reflections/independent reflections (R_{int})	8311/4653 (0.0636)
Coverage for θ = 25.99, %	100.0
The number of reflections with $I \ge 2\sigma(I)$	2629
Absorption correction	Empirical
(T_{min}/T_{max})	0.1334/0.4187
Number of refined parameters	272
GOOF on F^2	0.982
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0408$, $wR_2 = 0.0989$
R (all data)	$R_1 = 0.11492$, $wR_2 = 0.1235$
Extinction coefficient	0.0007(1)
Residual electron density (max/min), e Å^{-3}	3.069/–1.461

For $C_6H_{15}AgN_3O_4Re$ (**I**)

anal. calcd., %:	C, 14.79;	H, 3.08;	N, 8.62.
Found, %:	C, 15.03;	H, 3.97;	N, 8.70.

The above description of the synthesis reflects only the procedure, while the real formation of **I** occurs possibly via an intermediate step. The appearing turbidity of the reaction mixture is due to formation of an emulsion rather than to precipitation of a solid. With time, the reaction mixture becomes transparent, and thick syrup-like phase immiscible with the solution is deposited at the bottom of the vessel. After a long period of time, this phase is converted to crystals of **I**. Heating of the reaction mixture to 4°–50°C both in the absence of ammonia and after addition of ammonia results in the formation of silver metal.

X-ray diffraction. The experimental data for the crystals of **I** were collected on a CAD-4 Enraf-Nonius automated diffractometer. The structure was solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [7]. The hydrogen atom positions calculated geometrically were refined using the riding model. Note that the crystals tend to twinning and this affects the accuracy of the experiment.

The key crystal data and X-ray experiment details for the structure of **I** are summarized in Table 1, selective bond lengths are in Table 2, and the geometrical

Table 2. Selected bond lengths (*d*) and bond angles (ω) for **I***

Bond	*d*, Å	Bond	*d*, Å
Ag(1)–N(1)	2.209(9)	Ag(2)–N(4)$^{\#1}$	2.223(8)
Ag(1)–N(2)	2.178(9)	Ag(2)–N(6)	2.237(13)
Ag(1)–N(5)	2.562(10)	Ag(2)–N(3)	2.454(9)
Angle	ω, deg	Angle	ω, deg
N(1)Ag(1)N(2)	161.4(4)	N(6)Ag(2)N(4)$^{\#1}$	142.1(4)
N(2)Ag(1)N(5)	117.3(3)	N(4)$^{\#1}$Ag(2)N(3)	140.6(3)
N(1)Ag(1)N(5)	77.7(3)	N(3)Ag(2)N(6)	76.8(4)

* Symmetric codes of atoms: $^{\#1}$ $x, -y + 5/2, z + 1/2$.

Table 3. Geometric parameters of hydrogen bonds in structure **I**

A–H···B bond	Position of atom B	Distance, Å			AHB ange, deg
		A···B	A–H	H···B	
N(1)–H(1*C*)···O(5)	x, y, z	3.085(9)	0.90	2.26	152
N(1)–H(1*D*)···O(1)	$-x, y - 1/2, -z + 1/2$	3.000(9)	0.90	2.16	139
N(2)–H(2C)···O(1)	x, y, z	2.974(8)	0.91	2.07	171
N(4)–H(4*C*)···O(2)	$x, -y + 5/2, z - 1/2$	3.185(10)	0.91	2.07	137
N(6)–H(6*D*)···O(6)	$-x + 1, y + 1/2, z + 3/2$	3.083(10)	0.90	2.62	113

parameters of hydrogen bonds are given in Table 3. The full set of crystallographic data is deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1034044; http://www.ccdc.cam.ac.uk/deposit/).

The photoluminescence (PL) spectra were measured at room temperature on a Perkin Elmer LS-55 spectrometer (λ_{excit} = 200–800 nm, λ_m = 200–900 nm, instrument resolution 0.5 nm, slit size *d* = 10 nm) using the attachment for solid samples. The UV/Vis spectra were recorded at room temperature on a Cary5000 spectrophotometer (λ = 190–2500 nm, resolution 0.05 nm, standard deviation 0.005).

RESULTS AND DISCUSSION

The structure of **I** consists of cationic zigzag-like polymeric chains $[Ag(L)]^+_\infty$, extended along the [001] direction (Fig. 1). The crystallographically independent fragment of the structure is presented in Fig. 2. The ligand L functions as a tridentate bridge between silver atoms. The nitrogen atom of the NH_2 group and one heterocyclic N atom of the piperazine ring form an AgN_2C_2 chelate ring upon coordination to Ag, while the other piperazine nitrogen (NH) is bonded to the other silver atom. Both piperazine rings of ligands L(1) and L(2) have a chair conformation. Four

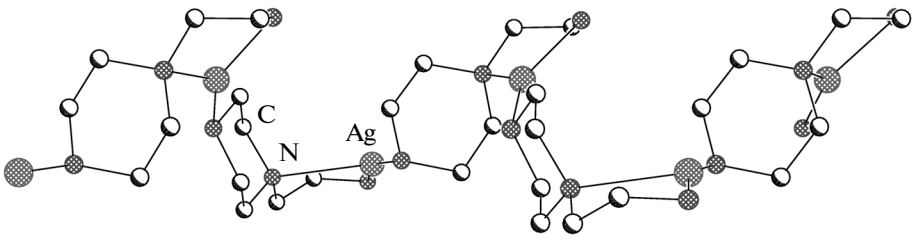

Fig. 1. 1D-zigzag-like chains in $[Ag(C_6H_{15}N_3)]^+_\infty$ in the structure.

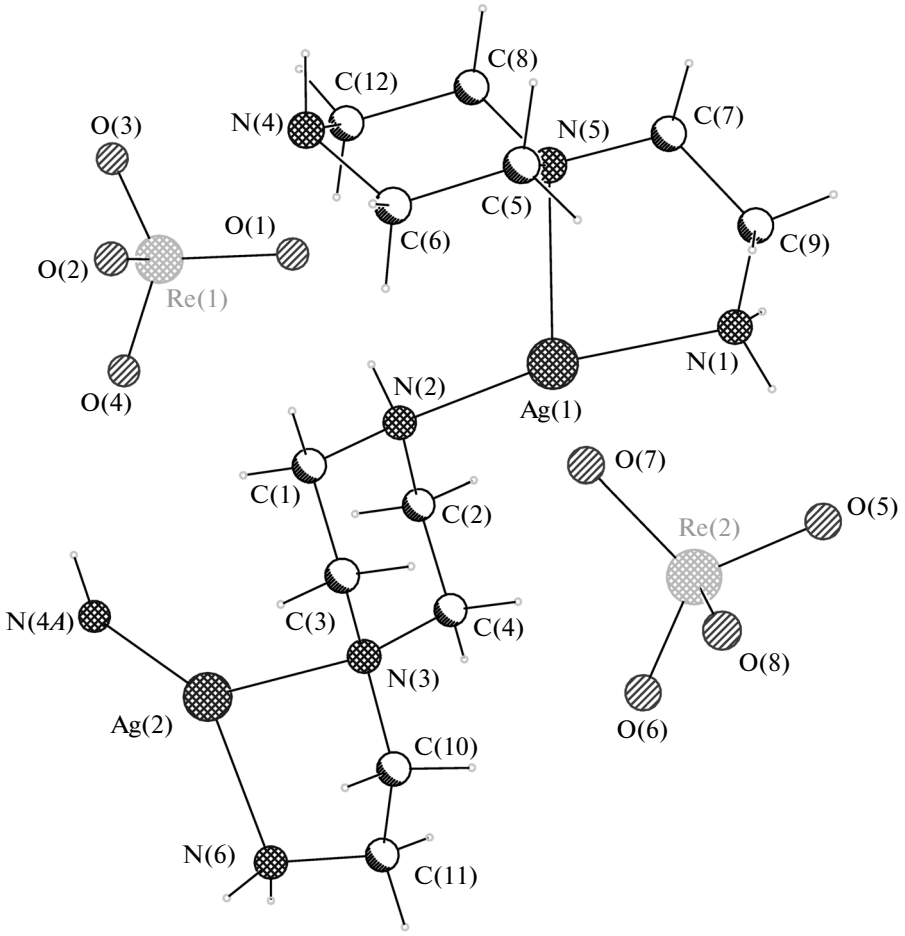

Fig. 2. Fragment of the structure of $[Ag(ReO_4)(C_6H_{15}N_3)]$.

C atoms of the piperazine ring are coplanar (≤0.002 Å), the N atoms being displaced from their plane (Δ_{aver} ± 0.69 Å). The Ag^+ ions coordinated by three nitrogen atoms (2 + 1) have a T-shaped coordination. As can be seen from Table 2, the minimum NAgN angles are at the nitrogen atoms of the chelate ring. Note that the degrees of distortion of the T-shaped coordination of Ag(1) and Ag(2) atoms are different, probably due to the steric effect of packing of the structural units.

The tetrahedral ReO_4^- anions are slightly distorted. The deviation of the bond length from the average value for Re(1)–O (1.67 Å) and Re(2)–O (1.71 Å) does not exceed 0.04 Å, and the deviations of the ORe(1)O (109°) and ORe(2)O (110°) angles from the average value are less than 4°. The ReO_4^- anions are involved in the N–H···O hydrogen bonds as proton acceptors (Table 3). As a result, a 3D supramolecular assembly is formed in **I** (Fig. 3). The shortest bond between the perrhenate oxygen atom and silver, Ag(2)···O(8) is 2.726(9) Å; the other Ag(2)···O bonds are longer than 3 Å.

The PL spectrum of compound **I** (Fig. 4) is superposition of several peaks in blue and green spectral regions; the most intense peaks are at ~420 and ~485 nm (curve *1*). Presumably, the emission of the complex is largely caused by intraligand $\pi \rightarrow \pi^*$ transitions. Figure 4 also shows the excitation spectrum (curve *2*) recorded for the emission band at 420 nm. The UV/Vis spectrum of compound **I** dissolved in acetonitrile is shown in Fig. 5; it can be seen that intense absorption occurs in the UV region at wavelengths of less than 300 nm.

As shown above, the ligand L in **I** performs both the chelating and bridging functions. Similar properties of L are observed in Hg^{II} compounds [3], the structure of which, however, differs markedly from the structure of **I**. In **I**, zigzag-like polymeric chains are formed through the nitrogen atoms of the ligand L functioning as the tridentate bridge between the silver atoms. The ReO_4^- anions are involved in the N–H···O hydrogen bonds, thus combining chains into a supramolecular

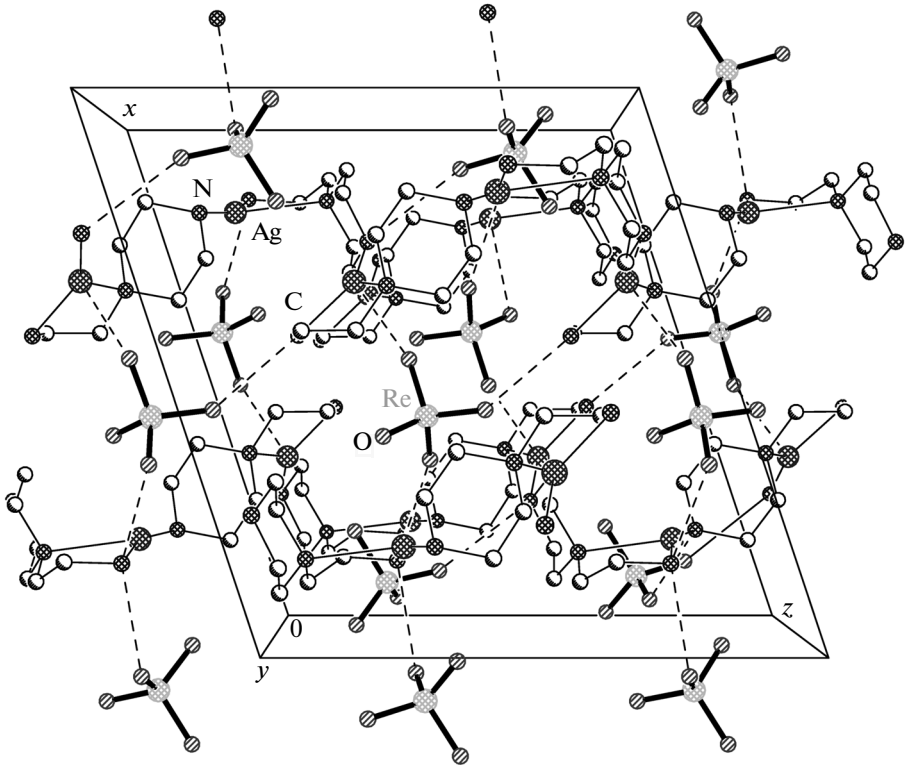

Fig. 3. Packing of structural units in the crystal of **I** along the [010] direction.

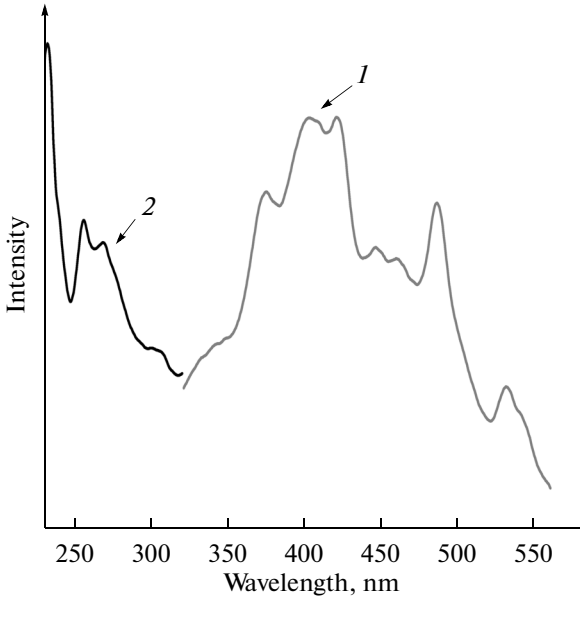

Fig. 4. (*1*) Luminescence spectrum at λ_{exit} = 255 nm and (*2*) excitation spectra at λ_m = 420 nm for compound **I**.

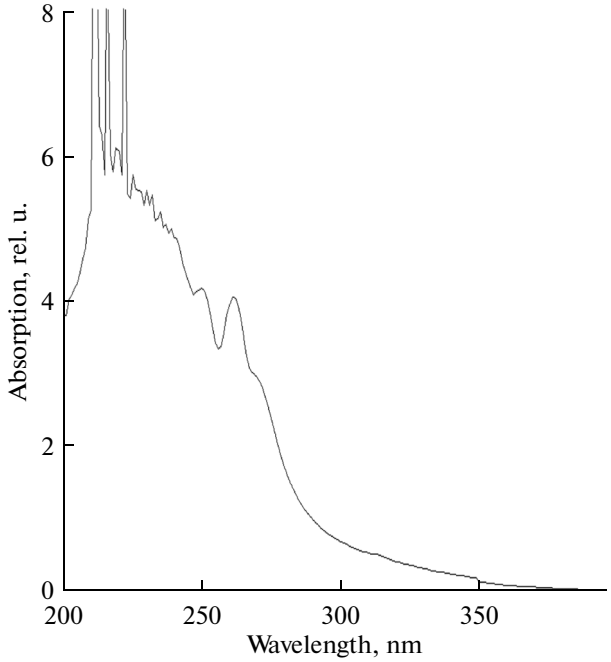

Fig. 5. Optical absorption of a solution of **I** in acetonitrile.

framework. In one of the two compounds of $HgCl_2$ with L, a discrete mononuclear complex is formed, while in the other one, the complex is tetranuclear: $[Hg_4^{II}(\mu_3\text{-}L)_2(\mu_2\text{-}Cl)_2Cl_6]$. Apart from L, chlorine atoms are also involved in its formation. In $[M^{II}(L)_2(Sac)_2]$, the ligand L has only the chelating function [4, 5]. Note that the Sac^{2-} and Cl^- ions are incorporated in the metal coordination sphere.

Considering the X-ray diffraction data together with the observed formation process of **I**, one can suggest that in the early stage of the reaction, L is coordinated to the silver atom only via two terminal nitrogen atoms belonging to the piperazine NH group and the NH_2 group. The formation of such a 1D polymer may account for the appearance, during the synthesis, of the syrup-like product, which is then converted to the crystals of **I**. Our attempts to prepare the complex of $AgNO_3$ with L in MeCN were unsuccessful both at 1 : 1 and 1 : 2 molar ratios. In this case, no phase separation was observed and, after complete removal of the solvent, the reaction product occurred as a transparent film from which silver metal was evolved upon storage in the dark.

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