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Coordination Polymer of Silver(I) Perrhenate with Quinoxaline: Synthesis, Crystal Structure, and Luminescence Properties

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Abstract—Silver compound [Ag(Quinox)](ReO$_4$) (**I**) (Quinox is quinoxaline, $C_8H_6N_2$) is synthesized, and its crystal structure is determined. The crystals are monoclinic: space group $P2_1/c$, $a = 7.217(1)$, $b = 15.238(1)$, $c = 9.446(1)$ Å, $\beta = 93.77(2)°$, $V = 1036.6(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.128$ g/cm^3. The structure includes cationic polymer chains $[Ag(Quinox)]^{+}_{\infty}$. The Ag$^+$ ion has an almost linear geometry (Ag(1)–N(1) 2.28(1) Å, Ag(1)–N(2) 2.23(1) Å, angle N(1)Ag(1)N(2) 169.0(5)°). The 3D supramolecular structure is formed due to a weak interaction of the oxygen atoms of the ReO_4^- anions with the silver ions. The compound is luminescent.

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INTRODUCTION

It is well known that silver is biologically active and is used as an antimicrobial agent in the metallic form and in the composition of various salts. Coordination compound [Ag(Quinox)]NO$_3$ was shown [1] to be an active antimicrobial agent. The study of its properties and structure showed that [Ag(Quinox)]NO$_3$ consisted of cationic coordination polymer [Ag(Quinox)]$^+$ and NO_3^- anion. Polymerization in the cation occurs due to the bridging properties of quinoxaline using both nitrogen atoms of the heteroaromatic cycle. In this respect, quinoxaline (Quinox) can be considered as a close analog of pyrazine and its substituted derivatives and various N-ligands containing conjugated aromatic rings (phenazine, phthalazine, naphthyridine, etc.), which can exhibit monodentate and bidentate bridging properties and are interesting as promising luminescent materials. The structures of complexes [Ag$_2$(Phtz)$_4$](NO$_3$)$_2$, [Ag$_2$(Naphthyridine)$_2$](ClO$_4$)$_2$, and [Ag(Quinox)]ClO$_4$ are presented [2].

Numerous studies of the syntheses and structures of coordination silver polymers with pyrazine derivatives show that these compounds include polymer structures of various composition due to bridging ditopic N-ligands [3–7]. The introduction of coordinating anions (for example, $CH_3CO_2^-$, $CF_3CO_2^-$, and $CH_3SO_3^-$) into these polymers results in the formation of 2D and 3D polymer compounds.

The results of synthesis and the crystal structure and photoluminescence spectra of the coordination silver compound Ag(Quinox)](ReO$_4$) (**I**) are presented in this work.

EXPERIMENTAL

Quinoxaline (Aldrich) and AgReO$_4$ synthesized by the reaction of NH$_4$ReO$_4$ with AgNO$_3$ [5] were used.

Synthesis of compound I. Weighed samples of AgReO$_4$ (0.30 g, 0.84 mmol) and quinoxaline (0.11 g, 0.83 mmol) were separately dissolved in 6 mL of acetonitrile each, and the solutions were mixed together. The obtained solution was filtered and kept for a day in a dark place with the slow evaporation of the solvent. The flesh-colored prismatic crystals formed were separated from the mother liquor, washed with a minor amount of acetonitrile, and dried in air. According to the chemical analysis data, the crystals corresponded to the composition AgReO$_4$($C_8H_6N_2$).

Selected crystallographic data and experimental characteristics for structure **I**

Parameter	Value
M	488.2
Crystal size, mm	0.25 × 0.15 × 0.10
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell parameters:	
a, Å	6.217(1)
b, Å	15.238(1)
c, Å	9.446(1)
β, deg	93.77(1)
V, Å^3	1036.6(2)
Z	4
ρ_{calcd}, g/cm^3	3.128
μ_{Mo}, mm^{-1}	13.554
F(000)	888
Temperature, K	293
Radiation (λ, Å)	MoK_α (0.71073), graphite monochromator
Scan mode	ω
θ Range, deg	2.54–31.96
Index ranges	$-1 \le h \le 10$, $-1 \le k \le 22$, $-14 \le l \le 14$
Total number of reflections/independent	4250/3336
R_{int}	0.1059
Completeness to θ = 31.96, %	93.0
Number of reflections with $I \ge 2\sigma(I)$	1524
Number of refined parameters	146
Goodness-of-fit for F^2	0.917
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0685$ $wR_2 = 0.1911$
R (all data)	$R1 = 0.1816$ $wR_2 = 0.2476$
Extinction coefficient	0.013(2)
Residual electron density (max/min), e/Å^3	4.155/–2.124

For $C_8H_6N_2O_4AgRe$

anal. calcd., %:	N, 5.74;	C, 19.67;	H, 1.23.
Found, %:	N, 5.68;	C, 19.59;	H, 2.59.

X-ray diffraction analysis. An experimental material for crystals **I** was obtained on an Enraf-Nonius CAD4 automated diffractometer. The structure was solved by a direct method and refined by the least-squares method in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELX-97) [8]. The positions of all hydrogen atoms were calculated geometrically and included into refinement by the riding model. The unit cell parameters and selected experimental characteristics are presented in the table. The tendency of the crystals to twinning, which affects the experimental accuracy, should be mentioned.

Photoluminescence spectra (PL) were recorded on an LS55 spectrometer (PerkinElmer) in the visible spectral range at room temperature (resolution 0.5 nm, gap width varying from 10 to 15 nm). An attachment for measuring luminescence of solids was used in this study.

RESULTS AND DISCUSSION

Structure **I** includes cationic polymer chains $[Ag(Quinox)]_\infty^+$ extended along the direction [100]. The Ag^+ ion has an almost linear geometry: (Ag(1)–N(1) 2.28(1) and Ag(1)–N(2)$^{\#1}$ 2.23(1) Å, angle N(1)Ag(1)N(2) 169.0(5)°) (Fig. 1). Two oxygen atoms of the ReO_4^- anion act as bidentate bridges between a pair of chains (Ag(1)–O(3)$^{\#1}$ 2.56(2) and Ag(1)–O(2)$^{\#2}$ 2.56(2) Å, angle O(3)$^{\#1}$Ag(1)O(2)$^{\#2}$ 74.6(9)° ($^{\#1}$*x*, *y*, *z* – 1; $^{\#2}$ –*x*, –*y* + 1, –*z* + 1) to form the metallocycle $[Ag_2O_4]$ (Fig. 2). The third O(1) atom of perrhenate has weak contacts with the silver atoms (Ag(1)–O(1)$^{\#3}$ 2.71(4) Å; $^{\#3}$ –*x*, 1/2 – *y*, 1/2 – *x*) joining doubled chains into a 3D spuramolecular framework. There is a π–π stacking interaction with the horizontal shift of the aromatic groups, the distance between which is 3.45 Å, along the direction [100] (Fig. 3) between the pairs of parallel centrosymmetric quinoxaline molecules (the dihedral angle between pairs of the rings is 0°). The angle between the normal to the ring plane and the vector between the centers of the rings corresponds to the horizontal shift of the aromatic groups, being 16°. The tetrahedral anion ReO_4^- is

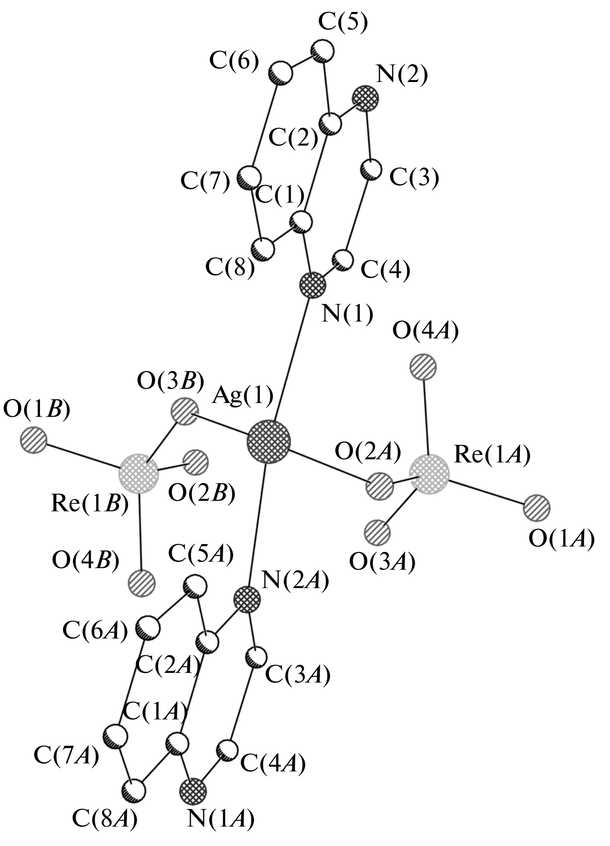

Fig. 1. Coordination mode of the Ag^+ ion in structure **I**.

insignificantly distorted. The deviation from the average value of the Re–O bond length (1.72 Å) does not exceed 0.02 Å, and that from the average value of the angle OReO (109°) is less than 2°.

The luminescence spectrum of quinoxaline (Fig. 4) contains two bands: a band at 550 nm (curve *1*) and a broader but less intense band near 615 nm (curve *2*). The luminescence spectrum of compound $AgReO_4L$ exhibits these two bands assigned to intraligand transitions in quinoxaline and also an intense band shifted to the blue range relative to uncoordinated quinoxaline with a maximum at 445 nm (Fig. 4). This band is probably attributed to the ligand-to-metal charge transfer (LMCT) and electron transitions (*ds*/*dp*) in the silver ion [9, 10].

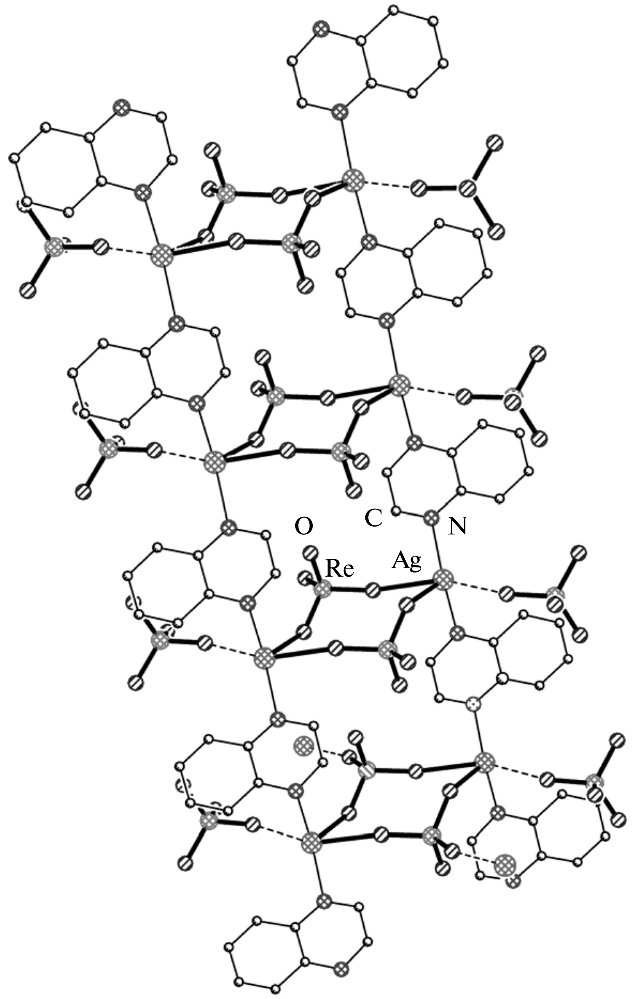

Fig. 2. Doubled chains $[Ag(Quinox)]_\infty^+$, joined by perrhenate ions in structure **I**.

A comparison of the studied structure **I** with the structure $[Ag(Quinox)]NO_3$ [1] shows that quinoxaline performs a bidentate bridging function in both cases and favors the formation of 1D cationic polymer chains $[Ag(Quinox)]_\infty^+$. In structure **I**, two oxygen atoms of the ReO_4^- anion are bidentate bridges between the pair of chains with the formation of the metallocycle $[Ag_2O_4]$. Also note that hydrogen bonds and the π–π stacking interaction play a significant role in the formation of these compounds along with the donor–acceptor bonds Ag–N. For example, the π–π stacking interaction with the horizontal angular shift of the aromatic groups is observed in compound **I** between the pairs of parallel centrosymmetric quinoxaline molecules. The 3D supramolecular structure is formed due to the weak interaction of one of the oxygen atoms of the ReO_4^- anions with the Ag^+ ions.

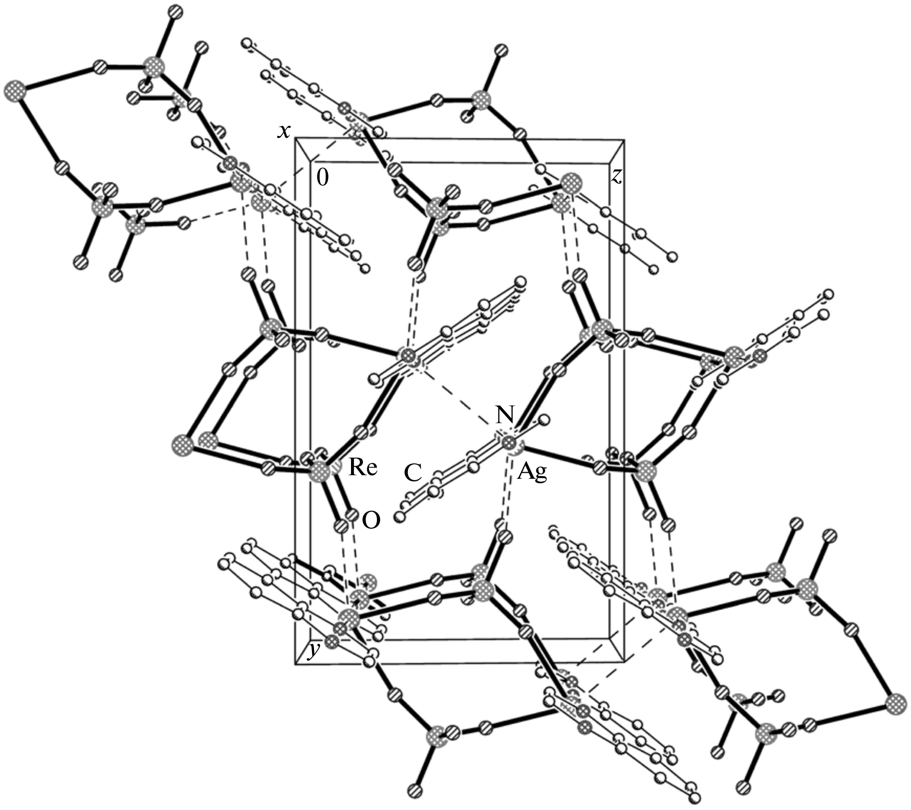

Fig. 3. General view of structure **I** along the direction [100].

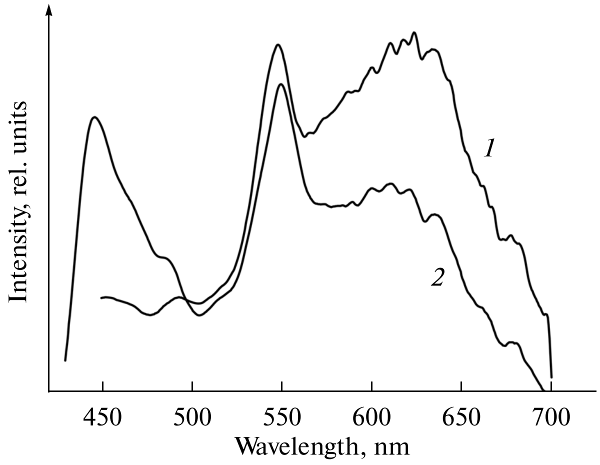

Fig. 4. Photoluminescence spectra of (*1*) quinoxaline and (*2*) [Ag(Quinox)](ReO_4)] at room temperature and at λ_{exc} = 400 and 405 nm, respectively.

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