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Binuclear Complex of Silver(I) Perrhenate with Phthalazine: Synthesis, Crystal Structure, and Luminescence Properties

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Abstract—Silver compound $Ag_2(Phtz)_4](ReO_4)_2$ (**I**) (Phtz is phthalazine, $C_8H_6N_2$) is synthesized, and its crystal structure is determined. The crystals are triclinic: space group $P\bar{1}$, $a = 9.651(2)$, $b = 9.655(2)$, $c = 10.884(2)$ Å, $\alpha = 115.752(2)°$, $\beta = 94.582(2)°$, $\gamma = 106.000(2)°$, $V = 854.3(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.404$ g/cm^3. The Ag atom forms a triangular coordination mode (Ag(1)–N(11) 2.34(2), Ag(1)–N(12*A*) 2.24(2), and Ag(1)–N(21) 2.28(1) Å) by the nitrogen atoms of one monodentate and two bridging phthalazine molecules. Their interaction results in the formation of an almost planar centrosymmetric binuclear cationic complex $[Ag_2(Phtz)_4]^{2+}$ (Ag(1)···Ag(1*A*) 3.452(7) Å). The oxygen atoms of the ReO_4^- anion are randomly disordered over three positions each. The luminescence spectrum contains an emission band in the green region.

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INTRODUCTION

Oxygen-containing compounds of metals with the d^{10} electron configuration (Ag^+, Cu^+) in combination with d^0 transition metals (Re, W, Nb) have recently been studied to reveal whether they can be used as photocatalytic materials [1–4]. The photocatalytic properties of these materials can be modified due to structural diversity of the compounds containing a combination of d^0 and d^{10} transition metals and organic donor ligands. The structures of a series of compounds based on $MReO_4$ (M = Cu^+, Ag^+) and organic N-donor ligands were thus synthesized and studied. It was found that these compounds included dimers, trimers, and chain and layered structures. In the latter case, the $AgReO_4$ layers are linked by the bidentate-bridging ligands [5–9].

Coordination compounds based on d^{10} metals and conjugated organic N-donor ligands have various structural architectures (from discrete to polymer) and are interesting as promising luminescent materials. In particular, silver salts are used for the construction of these compounds, as well as various conjugated ligands (phenazine, quinoxaline, phthalazine, etc.), which can manifest both the monodentate and bidentate-bridging properties. The structures of complexes $[Ag_2(Phtz)_4](NO_3)_2$ (**II**), $[Ag_2(naphthyridine)_2](ClO_4)_2$ (**III**), and [Ag(quinoxaline)]ClO_4 (**IV**) were presented [10]. It is shown that in compound **II** each Ag atom forms a triangular coordination mode by the N atom of one monodentate and two bidentate-bridging phthalazine molecules (Phtz), affording the binuclear silver complex. In compound **III**, the centrosymmetric binuclear silver complex is formed due to two bridging naphthyridine molecules with the shortened Ag–Ag distance (2.756 Å) in the dimer. The linear polymer –L–Ag–L–Ag–L– (L are quinoxaline molecules) is observed in compound **IV**.

The synthesis of the coordination compound of silver perrhenate with pyridazine molecules $[AgReO_4(Pda) \cdot 0.5H_2O]$ (**V**) (Pda is pyridazine, $C_4H_4N_2$) was described [4]. Compound **V** is based on the trimeric cationic complex $[Ag_3(Pda)_3]^{3+}$ weakly linked to the ReO_4^- anions.

The results of the synthesis, crystal structure, and photoluminescence spectra of the coordination silver compound $[Ag_2(C_8H_6N_2)_4](ReO_4)_2$ (**I**) are presented in this work.

EXPERIMENTAL

Synthesis of complex I was carried out via the reaction of $AgReO_4$ (obtained by the interaction of NH_4ReO_4 with $AgNO_3$ [8]) and phthalazine (Aldrich). Weighed samples of $AgReO_4$ (0.25 g, 0.69 mmol) and phthalazine (0.18 g, 1.38 mmol) were separately dissolved in acetonitrile (5 mL). The solutions were mixed, and the precipitated finely crystalline reaction product was decanted from the solution. Then the solid phase was dissolved in acetonitrile with the addition of an aqueous solution of NH_4OH and filtered. In several hours, the formed finely crystalline phase was again filtered off from the solution, and the filtrate was kept in the dark at room temperature under the conditions of slow evaporation of the liquid phase.

Crystallographic data and the main experimental characteristics for structure **I**

Parameter	Value
FW	1236.73
Color, habitus	Colorless block
Crystal size, mm	0.25 × 0.12 × 0.08
Crystal system, space group	Triclinic, $P\bar{1}$
Cell parameters:	
a, Å	9.651(2)
b, Å	9.655(2);
c, Å	10.884(2);
α, deg	115.752(2)
β, deg	94.582(2)
γ, deg	106.000(2)
V, Å^3	854.3(2)
Z	1
ρ_{calcd}, g/cm^3	2.404
μ_{Mo}, mm^{-1}	8.254
F(000)	580
T, K	150(2)
Radiation (λ, Å)	MoK_α (0.71073), graphite monochromator
Scan mode	ω
Scan increment, deg	0.5
Time per increment, s	1
θ Range, deg	2.14–26.00
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 11$, $-13 \le l \le 13$
Total number of reflections/independent (R_{int})	6669/3290 (0.0329)
Completeness to θ = 26.00, %	97.9
Number of reflections with $I \ge 2\sigma(I)$	2549
Absorption correction	Semiempirical, by equivalents
(T_{min}/T_{max})	0.2321/0.5580
Number of refined parameters	309
Goodness-of-fit for F^2	1.134
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0663$, $wR_2 = 0.1289$
R (all data)	$R_1 = 0.0887$, $wR_2 = 0.1431$
Extinction coefficient	0.0031(4)
Residual electron density (max/min), e/Å^3	2.947/–3.460

The precipitated crystals were separated from the solution, washed with a minor amount of acetonitrile, and dried in air.

For $C_{32}H_{24}Ag_2N_8O_8Re_2$			
anal. calcd., %:	N, 9.06;	C, 31.07;	H, 1.94.
Found, %:	N, 9.17;	C, 30.90;	H, 2.71.

X-ray diffraction analysis. The experimental material for crystals **I** was obtained on a Bruker SMART APEX II automated diffractometer. The structure was solved by a direct method (SHELX-97) [11] and refined by least squares in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELX-97) [12]. The positions of all hydrogen atoms were calculated geometrically and included into the refinement by the riding model. The unit cell parameters and the main experimental characteristics are given in the table. Note that the crystals are prone to twinning, which affects the experimental accuracy.

The full crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC 995386; http://www.ccdc.cam.ac.uk/services/structure deposit/).

The emission spectrum was recorded at room temperature on a PerkinElmer LS-55 spectrometer (λ_{exc} = 200–800 nm, λ_{em} = 200–700 nm, instrumental resolution 0.5 nm, slits d = 10–12 nm, and an attachment for solid-state samples). The phosphorescence regime with different delay times in the range from 0.1 to 1.5 ms was used.

RESULTS AND DISCUSSION

Structure **I** includes the centrosymmetric binuclear complex $[Ag_2(Phtz)_4]^{2+}$ (Fig. 1). The Ag(1)···Ag(1*A*) distance is 3.452(7) Å. The Ag^+ ion coordinated by three nitrogen atoms of one monodentate and two bidentate-bridging phthalazine molecules has a triangular coordination mode (Ag(1)–N(11) 2.34(2), Ag(1)–N(12*A*) 2.24(2), Ag(1)–N(21) 2.28(1) Å; angles N(11)Ag(1)N(21) 105.9(5)°, N(11)Ag(1)N(12*A*) 124.8(5)°, N(21)Ag(1)N(1*A*) 128.8(5)°). The minimum angle is observed between two bridging Phtz molecules, and the bridging and monodentate Phtz molecules form the maximum angle. Binuclear cationic complex **I** contains metallocycle Ag_2N_4 consisting of two silver ions and four nitrogen atoms. The oxygen atoms of the ReO_4^- anions are randomly disordered over three positions each (Re–O_{av} 1.70 ± 0.01 Å). The ReO_4^- anion is weakly bound to the Ag^+ ion (Ag^+ (Ag(1)···O(1) 2.59(2), Ag(1)···O(5) 2.62(2), Ag(1)···O(9) 2.68(5) Å). As can be seen from Fig. 1, only one oxygen atom in each position has weak contacts with the silver atom. Probably, this orientation of the perrhenate ion induces a

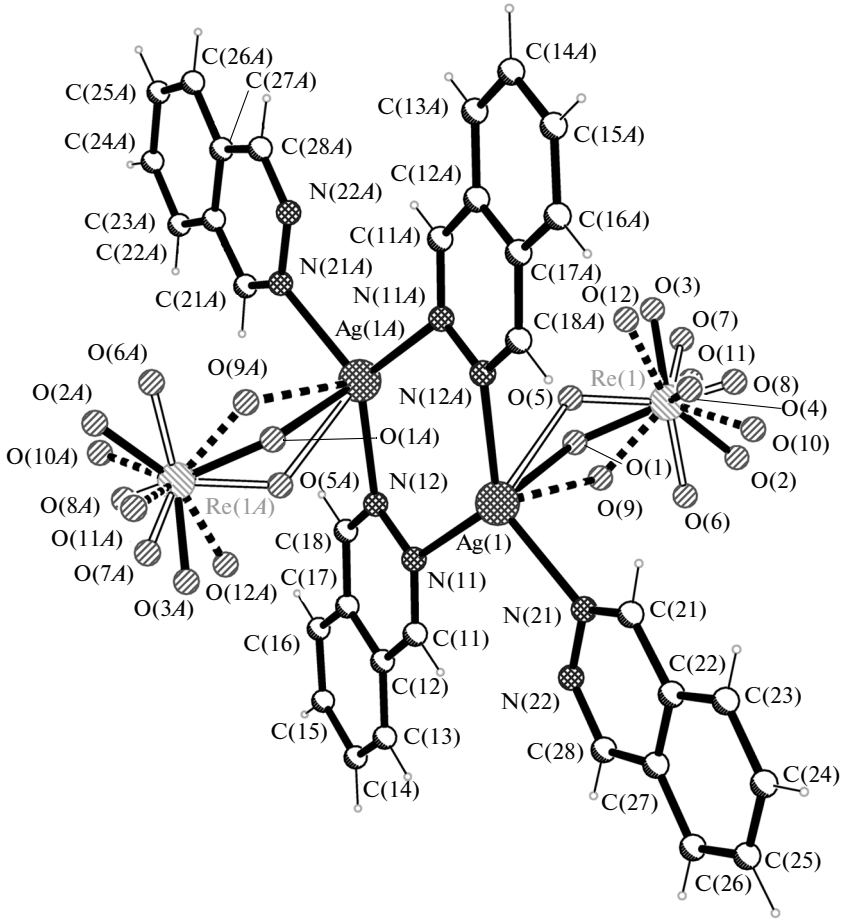

Fig. 1. Structure of the polynuclear complex in compound **I**.

noticeable distortion of the Ag^+ polyhedron. Note a similarity between structural motives in compound **I** and isotypical silver nitrate complex **II** [10].

Figure 2 shows the photoluminescence spectrum upon the excitation at a wavelength of 420 nm with a delay time ($\boldsymbol{\tau_d}$) of 0.1 ms (the intensity decreased with an increase in τ_d to 1.5 ms). As can be seen from the presented plot, there is a broad emission band with a maximum at 550 nm in the green spectral region, which can be decomposed (with a high degree of convergence) to two Gaussian bands with $\lambda_{max} = 547$ and 564 nm. This luminescence is caused, most likely, by the electron transitions in the Ag^{1+} ion and/or the intraligand $\pi-\pi^*$ transition.

An analysis of the luminescence spectra of compound **I** and literature data suggests that coordination compound **I** is a "candidate" for the production of luminescence materials emitting in the green spectral region.

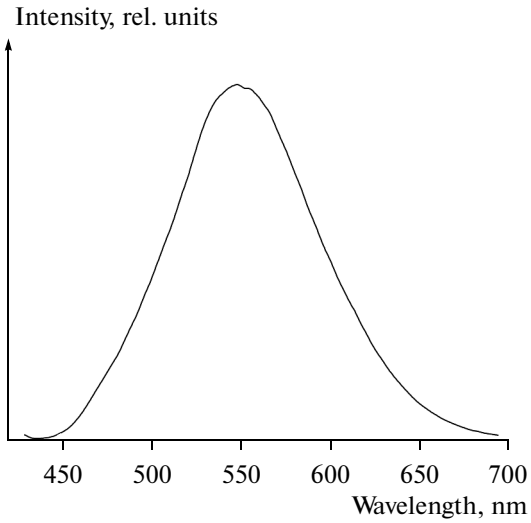

Fig. 2. Luminescence spectrum at $\lambda_{exc} = 420$ nm and $\tau_d = 0.1$ ms.

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