



Synthesis, structure, and photocatalytic properties of new dinuclear helical complex of silver(I) ions

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ABSTRACT

The 6',6''-(2-phenylpyrimidine-4,6-diyl)bis(6-methyl-2,2'-bipyridine) ligand **L** reacts with trifluoromethanesulfonate silver(I) to give dinuclear helical complex $[\text{Ag}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ in which metal ions are in approximately heavily flattened tetrahedron coordination geometry. The complex has been characterized by spectroscopic techniques, elemental analysis, transmission and scanning electron microscopies, and thermogravimetry. The solid state structure of complex has been determined by X-ray diffractometry. The methylene blue (MB) degradation was studied with UV–Vis spectrophotometry. A maximum degradation efficiency of 90% of the dye has been achieved. Photodegradation of the dye follows second-order kinetics. $[\text{Ag}_2\text{L}_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ is active photocatalyst of MB degradation under UV–Vis and sunlight irradiation.

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1. Introduction

Silver(I) ions are known to form various types of supramolecular complexes, including coordination frameworks [1], grids [2], helicates [3], cyclic helicates [4], metallamacrocycles [5], and clusters [6], depending on the nature of ligands, anions, solvents, and metal-to-ligand ratio. Specific physico-chemical properties of silver(I) compounds make them applicable in a variety of fields. For example, complexes displaying emission properties are promising luminescent materials [7]. Many silver(I) compounds exhibit anticancer [8], antimicrobial [9], and antifungal [10] activity. Therefore, these can be used as antibiotics and chemotherapeutic agents. Silver compounds play also important role in organic synthesis [11] as effective catalysts in many organic reactions including enantioselective cycloaddition of azometine and alkenes [12], Mannich reaction [13], or asymmetric protonation of silyl enolates [14]. Interestingly, silver complexes can be used as a catalyst for C–C bond formation in the synthesis of ethyl propionate from methane and diazoacetate [15]. Noteworthy, Zhang and co-workers reported a chiral dinuclear silver(I) complex with biaryl-based

nitrogen-donor ligand as an efficient catalyst in the enantioselective allylation reaction of benzaldehyde [16].

Frank and Bard [17] first examined the possibilities of using TiO_2 to decompose cyanide in water. Since then, there has been an increasing interest in environmental applications of TiO_2 such as air purification, deodorization, sterilization, anti-fouling, and mist removal [18–20]. Because of wide band gap of TiO_2 ($E_g = 3.20$ eV), all these photocatalytic reactions require UV illumination to proceed efficiently. UV light accounts for only about 2–3% of the total sunlight, whereas visible light accounts for 45%. Consequently, considerable efforts have been devoted to the development of photocatalysts that are capable to utilize visible light efficiently. Much attention has been focused to achieve the utilization of visible light via nonmetal or transitional metal ion doping of TiO_2 . It has been reported that the co-doped silver and nitrogen caused significant widening of the absorption spectrum of TiO_2 , from the region near 400 nm to entire visible region. The visible light response was enhanced along with silver doping content [21]. It has been found that Ag–ZnO powders reveal increased absorption in 400–700 nm region. Moreover, the absorption increased along with Ag loadings between 0 and 5 at.% [22]. As reported elsewhere, deposition of silver on the hollow $\text{SiO}_2/\text{TiO}_2$ hybrid spheres results in a significant enhancement in the photodegradation of rhodamine B under visible light irradiation [23].

After successful synthesis of grid-type [24,25] and helical [26] complexes of silver(I), we attempted to prepare silver(I) complex

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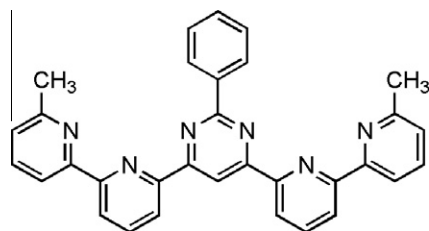


Fig. 1. The ligand L ($C_{32}H_{24}N_6$).

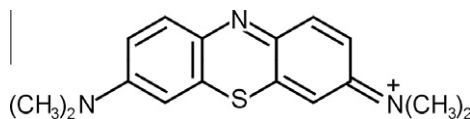


Fig. 2. Chemical structure of methylene blue.

with new N_6 -donor ligand. Herein, we report synthesis, crystal structure of helical silver(I) complex with ligand 6',6''-(2-phenylpyrimidine-4,6-diyl)bis(6-methyl-2,2'-bipyridine) $L-[Ag_2L_2](CF_3SO_3)_2 \cdot H_2O$ (Fig. 1) and its photocatalytic activity during photodecomposition of organic compounds under ultraviolet and sunlight. Methylene blue (MB) was selected as a model for the organic pollution, because it is considered by the International Organization of Standardization (ISO) as a standard method for testing and comparison of photocatalytic coatings efficiency and it is commonly adopted to evaluate the catalytic activity of a catalyst [27]. Chemical structure of MB is presented at Fig. 2.

According to our knowledge, synthesis route and properties of $[Ag_2L_2](CF_3SO_3)_2 \cdot H_2O$ have not been described before.

2. Experimental

2.1. General procedure

Trifluoromethanesulfonate silver(I) was used as supplied from Aldrich without further purification. Ligand 6',6''-(2-phenylpyrimidine-4,6-diyl)bis(6-methyl-2,2'-bipyridine) L was prepared in our laboratory [28]. NMR spectra were measured using a Varian Gemini (300 MHz) spectrometer. The instrument was calibrated against the residual protonated solvent signals (CD_3CN δ 1.94) and shifts are given in ppm. Mass spectra for acetonitrile solutions $\sim 10^{-4}$ M were determined using a Waters Micromass ZQ spectrometer. Microanalysis was obtained using a Perkin Elmer 2400 CHN microanalyzer. IR spectra in the 4000–400 cm^{-1} region were measured with a Perkin–Elmer 580 spectrophotometer. KBr pellets were used for each measurement.

Diffraction data were collected at 100(1) K by the ω -scan technique, on an Xcalibur diffractometer with graphite-monochromatized $Mo K\alpha$ radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz-polarization and absorption effects [29]. Unit-cell parameters were determined by a least-squares fit of 4367 reflections of highest intensity, chosen from the whole experiment. The structure was solved with SIR92 [30] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [31]. Scattering factors incorporated in SHELXL97 were used.

The morphology and chemical composition of the samples were examined using a scanning electron microscope (SEM JEOL JSM-6100) and a transmission electron microscope (TEM-FEI Tecnai F20). Suitable specimens were prepared on a copper grid.

The diffuse reflectance spectroscopy (DRS) spectra were recorded by a DR-UV-Vis spectrometer Jasco V650. The wavelength ranges from 250 to 800 nm.

Table 1
Crystal data, data collection, and structure refinement.

Compound	1
Formula	$(C_{64}H_{48}Ag_2N_{12}) 2(CF_3SO_3) \cdot H_2O$
Formula weight	1517.02
Crystal system	Triclinic
Space group	P-1
a (Å)	14.3401(15)
b (Å)	15.2967(10)
c (Å)	15.5717(15)
α	86.090(7)
β (°)	87.481(8)
γ	77.793(7)
V (Å ³)	3329.2(5)
Z	2
T (K)	100(1)
D_x ($g\ cm^{-3}$)	1.51
$F(000)$	1532
μ (mm^{-1})	0.73
Crystal size (mm)	$0.24 \times 0.18 \times 0.05$
Θ range (°)	2.91–28.06
$h\ k\ l$ range	$-27 \leq h \leq 10$ $-16 \leq k \leq 16$ $-20 \leq l \leq 16$
Reflections	
Collected	10,256
Unique (R_{int})	8565 (0.029)
With $I > 2\sigma(I)$	5334
No. of parameters	860
$R(F)$ [$I > 2\sigma(I)$]	0.134
$wR(F^2)$ [$I > 2\sigma(I)$]	0.331
$R(F)$ [all data]	0.180
$wR(F^2)$ [all data]	0.363
Goodness of fit	1.030
max/min $\Delta\rho$ ($e\ \text{Å}^{-3}$)	1.83/–1.29

The thermogravimetric (TG) analyses were carried out using STA 449 C TGA apparatus (Netzsch, Germany). Measurements were taken in nitrogen atmosphere ($30\ ml\ min^{-1}$) from room temperature to 800 °C. The temperature was increased linearly and the heating rate was $10\ ^\circ C\ min^{-1}$.

Methylene blue was employed as a model dye to evaluate the photocatalytic activity of the synthesized powder. Photodegradation experiments were performed at the 2×2 cm (glass) plates covered by 3.9 mg $[Ag_2L_2](CF_3SO_3)_2 \cdot H_2O$. On the every plate, 0.15 mg of MB was applied ($1\ g/dm^3$ MB solution). The plates were exposed to the sunlight and UV-Vis light (290–800 nm, $1800\ kJ/m^2$ in 1 h). With intervals of 30 min, the dye concentration was measured by UV-Vis spectroscopy. Blank reactions are conducted to ensure that the degradation of MB is due to the photocatalytic reaction and to eliminate surrounding interference.

2.2. Preparation of the complex $[Ag_2L_2](CF_3SO_3)_2 \cdot H_2O$

A mixture of $AgCF_3SO_3$ (20.6 mg, 0.08 mmol) and ligand L (40.2 mg, 0.08 mmol) in $CH_3CN:CH_2Cl_2$ 1:9 (20 mL) was stirred at room temperature for 48 h under the normal atmosphere. The product- H_2O was isolated by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH_3CN by the gradual addition of ether to obtain complexes as a white solid. Yield 82% (50.2 mg).

ESI-MS m/z (%) = 599 (100) $[Ag_2(C_{32}H_{24}N_6)_2]^{2+}$ 1H NMR (300 MHz, CD_3CN): δ = 9.74 (s, 2H), 8.49 (d, 4H, $J = 7.4$ Hz), 8.31 (m, 4H, $J = 4.2$ Hz), 8.15 (d, 8H, $J = 4.2$ Hz), 7.83 (m, 8H, $J = 8.1$ Hz), 7.50 (m, 6H, $J = 4.5$ Hz), 7.21 (d, 4H, $J = 7.8$ Hz), 1.88 (s, 12H, CH_3) ppm. IR (KBr) ν = $\nu(C-H)_{ar}$ 3059; $\nu_{as}(C-H)$ 2924; $\nu_s(CH_3)$ 2853; $\gamma(C-H)$ overtones 1991–1734; $\nu(C=C)$ 1599, 1564, 1537; $\nu(C=N)_{py}$ 1461, 1445; $\delta(CH_3)$ 1380; $\nu_{as}(SO_3)$ 1253; $\nu_s(F_3)$ 1231; $\nu_{as}(CF_3)$ 1171; $\rho(C-H)_{py}$ 1087, 1073; $\nu_s(SO_3)$ 1033; $\gamma(C-H)_{py}$ 994, 826, 790, 760, 740, 697, 643; $\delta(CF_3)$ 576; $\delta(SO_3)$ 518 cm^{-1} .

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