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Synthesis, crystal structure, photoluminescence and photochemistry of bis(triphenylphosphine) silver(I) flavonolate

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Abstract: The complex $\text{Ag(I)(flavonolate)(PPh}_3)_2$ has been prepared and characterized including the crystal structure. This compound shows in degassed solution two emission bands, a fluorescence at $\lambda_{\text{max}} = 505$ nm and a phosphorescence at $\lambda_{\text{max}} = 780$ nm. Both emissions originate from lowest-energy flavonolate intraligand excited singlet and triplet states, respectively. In the presence of oxygen, the phosphorescence disappears and the complex becomes light-sensitive. The flavonolate ligand undergoes a photooxidation by oxygen.

Keywords: crystal structure; flavonolate; photochemistry; photoluminescence; silver(I).

1 Introduction

Flavonol (or 3-hydroxyflavone) is a compound of biological importance. A variety of hydroxy derivatives such as quercetin or kaempferol are natural phytochemical compounds, which occur in many plants. Among other beneficial properties they act as antioxidants. As backbone they contain flavonol (structure 1).

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Owing to the adjacent carbonyl and hydroxy substituent, the flavonolate anion (deprotonated flavonol) forms chelate complexes with various main group and transition metal ions including Ru(II) [1, 2], Zn(II) [3] and Cu(I) [4, 5]. Accordingly, such complexes may modify the biological activity of flavonol and could be suitable as biomarkers or therapeutic agents for medical applications. In this context, we decided to prepare, characterize and explore the excited state properties of a silver flavonolate complex, because Ag^+ ions are well known to suppress undesired infections [6]. However, Ag^+ could be reduced thermally and in particular photochemically to metallic silver [7]. This induces an irreversible skin darkening (argyria) which should be avoided. In analogy to $\text{Cu(flavonolate)(PPh}_3)_2$ [4, 5] the corresponding Ag^+ complex was expected to be accessible by a simple procedure. The excited state behavior of the silver complex should be quite different from that of the Cu^+ compound [8]. In the case of Ag^+ , metal-centered ds, MLCT and LMCT transitions occur only at very high energies [9] and might not interfere with intraligand (IL) transitions at much lower energies.

2 Experimental

2.1 Synthesis of $\text{Ag(flavonolate)(PPh}_3)_2$

Ag(acetate) (0.17 g), flavonol (0.24 g) and PPh_3 (0.52 g) in molar ratio 1:1:2 were added to 10 mL acetonitrile. This mixture was stirred for 30 min. A solid product separated. It was collected by filtration and dried in a vacuum. The yield of the bright yellow product was ca. 80%. – Analysis for $\text{Ag(flavonolate)(PPh}_3)_2$ ($\text{C}_{51}\text{H}_{39}\text{AgO}_3\text{P}_2$): Calcd C 70.4, H 4.5; found C 69.8, H 4.6. This product contains a small amount of free flavonol which was removed by recrystallisation from diethyl ether.

2.2 X-ray crystallography

Clear, light yellow plate-shaped single crystals were obtained by recrystallisation from diethyl ether. A suitable

crystal of $0.18 \times 0.10 \times 0.04$ mm³ was selected and mounted on a MITIGEN holder with inert oil on an GV1000, TitanS2 diffractometer [10]. The crystal was kept at $T = 123.0(1)$ K during data collection (CuK α radiation, $\lambda = 1.54184$ Å).

The structure was solved with the SHELXT [11] structure solution program using the Intrinsic Phasing solution method and OLEX2 [12]. The model was refined with version 2016/6 of SHELXL [13] using least-squares minimization. Crystal data and further details of data collection and structure refinement are summarized in Table 1.

CCDC 1859110 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3 Results and discussion

The synthesis proceeds according to eq. (1)

The molecular structure of Ag(flavonolate)(PPh₃)₂ (Fig. 1), determined by single-crystal X-ray diffraction, confirms the composition expected according to the general analytical results and in analogy to Cu(flavonolate)(PPh₃)₂

Fig. 1: Molecular structure of Ag(flavonolate)(PPh₃)₂ in the solid state. Selected bond lengths and angles (Å, deg): Ag–O3 2.395(3), Ag–O2 2.307(3), O3–C9 1.255(5), O2–C1 1.297(5), C1–C9 1.472(6); O2–Ag–O3 71.80(11), Ag–O3–C9 112.4(3), Ag–O2–C1 114.8(3).

[4, 5]. The Ag(I) complex actually turns out to be isostructural to the previously determined Cu(I) complex [4, 5].

The silver ion is pseudo-tetrahedrally coordinated to two oxygen and two phosphorus atoms. Some bond distances within the flavonol(ate) ligand are of particular interest.

Generally, the CO bond distances for ketones and alcohols are approximately 1.22 and 1.42 Å, respectively, yielding a difference of $\Delta = 0.20$. For the silver complex the C9–O3 bond length of the keto substituent amounts to 1.26 Å, while the C1–O2 the bond length of the formally alcoholic substituent is only slightly longer with 1.30 Å and the difference is very small with $\Delta = 0.04$. There is apparently a considerable electron delocalization within the flavonolate ligand, which is coordinated to Ag⁺, while for the free flavonol [14] it is $\Delta = 0.11$ Å. This is relatively close to the difference between a keto and an alcoholic CO bond distance in general ($\Delta = 0.20$).

The mass spectra confirm the composition of the complex Ag(flavonolate)(PPh₃)₂. The FD spectrum shows the molecular ions as prominent signals at $m/z = 868.16944$, 870.19216, 869.18735, and 871.14312 reflecting the presence of the two silver isotopes ¹⁰⁷Ag and ¹⁰⁹Ag. The measured spectrum coincides with the simulated spectrum. The ESI-MS spectrum does not contain the peak of the molecular ion but displays only signals of fragments of the complex.

Table 1: Crystal data and numbers pertinent to data collection and structure refinement for Ag(flavonolate)(PPh₃)₂.

Formula	C ₅₁ H ₃₉ AgO ₃ P ₂
<i>M_r</i>	869.63
Crystal size, mm ³	0.18 × 0.10 × 0.04
Temperature, K	123.0(1)
Crystal system	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	9.31690(10)
<i>b</i> , Å	17.3953(2)
<i>c</i> , Å	24.9303(2)
<i>V</i> , Å ³	4040.46(7)
<i>Z</i>	4
<i>D_{calcd}</i> , g cm ^{−3}	1.43
μ (CuK α), mm ^{−1}	5.1
θ range data collection, deg	3.546–74.192
Refl. total/unique/ <i>R_{int}</i>	29324/8008/0.0761
<i>R₁</i> / <i>wR₂</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0356/0.0903
<i>R₁</i> / <i>wR₂</i> (all data)	0.0362/0.0910
<i>S</i> (GoF)	1.066
Flack <i>x</i>	−0.013(4)
$\Delta\rho_{\text{fin}}$ (max/min), e Å ^{−3}	1.07/−1.19

Fig. 2: Absorption spectrum of 0.8×10^{-4} M Ag(flavonolate)(PPh₃)₂ in diethyl ether in a 1-cm quartz cell.

3.1 Electronic spectra

3.1.1 Absorption

The absorption spectrum of Ag(flavonolate)(PPh₃)₂ is characterized by a long-wavelength band (Fig. 2) at $\lambda = 435$ nm ($\epsilon = 1.5 \times 10^4$ mol⁻¹ cm⁻¹), which is hardly solvent dependent. It is assigned to the lowest-energy, spin-allowed flavonolate IL transition. Flavonolate itself displays this band at 415 nm [15], while in the case of flavonol it is blue-shifted and appears at 345 nm.

3.1.2 Emission

The complex Ag(flavonolate)(PPh₃)₂ is luminescent in solution as well as in the solid state. In a degassed solution the emission spectrum (Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier) shows two bands (Fig. 3) at $\lambda_{\text{max}} = 505$ and 780 nm. An excitation maximum appears at 465 nm.

The green emission at $\lambda = 505$ nm is certainly a flavonolate IL fluorescence which overlaps with the corresponding spin-allowed absorption (Fig. 2). The long-wavelength emission at $\lambda_{\text{max}} = 780$ nm is suggested to originate from the lowest-energy flavonolate IL triplet. This phosphorescence is probably facilitated by the heavy-atom effect of silver [16]. While the fluorescence is not affected by oxygen, the phosphorescence is completely quenched in a solution saturated with air. This phenomenon is quite frequently observed for other complexes

Fig. 3: Excitation (exc) and emission (emi) spectrum of a degassed solution of Ag(flavonolate)(PPh₃)₂ in ether in 1-cm quartz cell; intensity (Int) in arbitrary units.

with a phosphorescence induced by a heavy-atom effect [17]. The triplet state lifetime under these conditions is in the microsecond range, which allows a phosphorescence quenching by oxygen in a diffusion-controlled process. In the solid state the luminescence of Ag(flavonolate)(PPh₃)₂ appears at $\lambda_{\text{max}} = 525$ nm (fluorescence) and 785 nm (phosphorescence) with an excitation at 450 nm.

3.1.3 Photochemistry

In degassed solution, Ag(flavonolate)(PPh₃)₂ is not light sensitive. However, in an air-saturated solution, the complex undergoes an efficient photochemical reaction as indicated by the disappearance of its absorption (Fig. 4) and fluorescence (Fig. 5).

Various metal flavonolate complexes have been shown to undergo a catalyzed [18] or photochemical oxidation [2, 19] by O₂. This leads to a C–C bond cleavage of the flavonolate ligand yielding CO and O-benzoylsalicylate. In the case of the photooxygenation, it has been assumed [2] that the flavonolate ligand acts as sensitizer, which generates singlet oxygen. ¹O₂ in turn could oxidize the flavonolate ligand. This mechanism is likely to apply also to the silver complex. Initially, the IL triplet is intercepted by ³O₂ as indicated by the phosphorescence quenching in aerobic solution. Subsequently, singlet oxygen attacks the flavonolate ligand. In this context, it is rather intriguing that the IL triplet is apparently so low in energy that an

Fig. 4: Changes of the absorption spectrum upon irradiation of 0.8 mM Ag(flavonolate)(PPh₃)₂ in air-saturated diethyl ether in a 1-cm quartz cell; $\lambda_{\text{irr}} > 400$ nm; irradiation time: upper spectrum 0 min, lower spectra 1.5, 3, 4.5, 6, and 9 min (lowest spectrum).

Fig. 5: Changes of the fluorescence spectrum of Ag(flavonolate)(PPh₃)₂ in air-saturated acetonitrile in a 1-cm quartz cell; intensity (Int) in arbitrary units; $\lambda_{\text{irr}} > 400$ nm; irradiation time: (a) 0 min, (b) 1 min, (c) 2 min and (d) 3 min.

intramolecular radiationless transition to a LMCT state does not occur and consequently a photoreduction to elemental silver is not observed. It follows that the generation of ¹O₂ could be utilized for a photodynamic therapy, while the concomitant release of Ag⁺ ions should suppress interfering infections.

In summary, the complex Ag(I)(flavonolate)(PPh₃)₂ is characterized by a flavonolate IL fluorescence and phosphorescence. The latter is quenched by oxygen, which subsequently oxidizes the flavonolate ligand.

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