A ligand substituted tungsten iodide cluster: luminescence vs. singlet oxygen production†

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Octahedral tungsten iodide clusters equipped with apical ligands (L) are synthesized to implement substantial photophysical properties. The \([\text{W}_6\text{I}_8(\text{CF}_3\text{COO})_6]^{2-}\) cluster reported herein is the first example of a family of ligand substituted \([\text{W}_6\text{I}_8\text{L}_6]^{2-}\) clusters. Such compounds are expected to exhibit a rich photochemistry in which the apical ligands play a crucial role. The versatile solid state and solution phase photophysical properties of (TBA)\(_2\)[W\(_6\)I\(_8\)(CF\(_3\)COO)\(_6\)] described herein parallel characteristics obtained in some photophysically active organic compounds, including a broad absorption in the UV/VIS region. Upon irradiation of this compound, a broad red emission is observed in the VIS/NIR region resulting from excited triplet states, and singlet oxygen (\(a^1\Delta_g\)) is generated in the presence of \(\text{O}_2\).

Introduction

Optical materials are an essential part of our daily life; they offer attractive and energy-efficient applications in photocatalysis,\(^1\) sensing,\(^2\) lighting,\(^3\) and solar energy harvesting,\(^4\) for example. Thus, photoactive materials and studies of the properties of such materials with an eye to new developments are important.

For the past decades, the electronic structure and photophysical properties of \(\text{Mo}_6\text{Cl}_{12}\) based compounds have been studied.\(^5\) The structure of the \([\text{Mo}_6\text{Cl}_{14}]^{2-}\) ion is based on an octahedral molybdenum cluster core carrying eight inner (\(i = \text{innen}\)) face-capping and six outer (\(a = \text{außen}\)) apical chloride ligands making up a \([\text{Mo}_6\text{Cl}_{8}i\text{Cl}_6a]^{2-}\) ion which resembles the prototypical structure for many cluster compounds. Cluster compounds of this type are remarkably stable in solution and in the solid state. However, their apical ligands are always more weakly bound, allowing a broad substitutional chemistry for terminal ligands (L).

Considerable attention has focused on the structures and photophysical properties of octahedral metal cluster compounds \([\text{M}_6\text{X}_8\text{L}_6]^{n-}\) with \(\text{M} = \text{Mo}, \text{X} = \text{halide}, \text{and} \text{M} = \text{Re}, \text{X} = \text{S, Se or Te}, \text{containing inorganic or organic ligands (L)}\).\(^6\)

Octahedral rhenium chalcogenide clusters, developed almost simultaneously in 1999 by the groups of Kitamura,\(^7\) Batail\(^8\) and Nocera\(^9\) are showing versatile potential in optical applications.\(^10\) Likewise, a number of ligand substituted octahedral molybdenum clusters, such as (TBA)\(_2\)[Mo\(_6\)I\(_8\)(CF\(_3\)COO)\(_6\)]\(^11\) and (TBA)\(_2\)[Mo\(_6\)I\(_8\)(CF\(_3\)COO)\(_6\)]\(^12\) (TBA = tetrabutyl ammonium), exhibit remarkable photophysical properties.\(^13\)

The aforementioned metal chalcogenide and metal halide compounds have broad absorption bands in the UV-VIS region and emit in the red VIS/NIR region of the electromagnetic spectrum. It is clear that the photoexcitation involves an \(S_0\) to \(S_m\) transition, followed by intersystem crossing (ISC) into triplet states.\(^14\) Phosphorescence quenching obtained in the presence of molecular oxygen is, at least partially, explained by energy transfer with the formation of singlet oxygen, \(O_2(a^1\Delta_g)\),\(^15\) as shown in Fig. 1.

![Fig. 1. Electronic transitions and singlet oxygen generation \((a^1\Delta_g)\) in \([\text{M}_6\text{X}_8\text{L}_6]^{2-}\) type clusters following a modified Jablonski-Diagram.\(^16\)](attachment://attachment.png)
The photophysical and electrochemical properties of \([\text{M}_6\text{X}_8\text{L}_6]^{2-}\) cluster compounds can be tuned by substitutions of inner ligands (X) as well as outer organic or inorganic ligands (L). The perspectives of ligand exchange reactions in \([\text{M}_6\text{X}_8\text{L}_6]\) clusters and the influence of apical ligands with respect to the \(S_0 \rightarrow S_1\) excitation, described as ligand → metal charge transfer (LMCT) potential and interest in \([\text{M}_6\text{X}_8\text{L}_6]\) cluster compounds regarding applications in the fields of oxygen sensing, photocatalysis, photoreduction of CO\(_2\), luminescent nanoparticles, organic synthesis, and photodynamic therapy.

Corresponding tungsten iodide compounds \([\text{W}_6\text{I}_8\text{L}_6]^{2-}\) remained absent until now. One reason is that there has been no appropriate synthesis available for the preparation of a binary tungsten iodide which could serve as a starting material (e.g. \([\text{W}_6\text{I}_{12}]\)), although particularly strong luminescence properties of tungsten iodides, among \([\text{W}_6\text{X}_8\text{X}_8]\) clusters with X, \(X' = \text{Cl}, \text{Br}, \text{I}\), have been observed. We here report the synthesis and photophysical characterization of a ligand substituted \([\text{W}_6\text{I}_8\text{L}_6]^{2-}\) cluster compound.

**Results and discussion**

The development of a new synthetic route for tungsten iodides based on a halide exchange reaction of WCl\(_6\) with SiI\(_4\) enable us to generate tungsten iodide in large scale, based on W\(_i\)I\(_{12}\) with \(n=0, \frac{1}{3}, \frac{2}{3}\). The octahedral cluster compound \(\text{Cs}_2[\text{W}_6\text{I}_{12}]\) is prepared by thermal conversion of singlet oxygen (\(\Phi_{\Delta}\)) in the presence of oxygen.

Corresponding tungsten iodide compounds \([\text{W}_6\text{I}_8\text{L}_6]^{2-}\) crystallizes with the triclinic space group P1. \([\text{W}_6\text{I}_8]\) ions are arranged in the \(bc\)-plane of the crystal, following the motive of a hexagonal closed packed layer, with a primitive stacking sequence along the \(b\)-axis direction. TBA ions can be approximated to occupy trigonal prismatic voids made up by the arrangement of clusters (Fig. 3).

![Fig. 2](image2.jpg) Exchange reaction of outer (a) iodide ligands in \([\text{W}_6\text{I}_8\text{I}_n]^{2-}\) by trifluoroacetate with the formation of \([\text{W}_6\text{I}_8\text{CF}_3\text{COO}]_{\text{aq}}^{2-}\).
Tungsten atoms in the centrosymmetric \([W_6I_8(CF_3COO)_6]\)^{2-} cluster are arranged to form an octahedral arrangement with W-W distances ranging between 264.67(4) and 265.80(5) pm. Triangular cluster faces are capped by inner iodide ligands with W-I distances ranging from 278.48(6) to 282.24(6) pm. Three crystallographically distinct trifluoroacetate ligands appear in \([TBA]_2[W_6I_8(CF_3COO)_6]\) forming W-O-C angles of 135.1(6)°, 136.8(6)° and 134.8(6)° with tungsten atoms of the cluster. C-C distances within trifluoroacetate ligands range from 149(1) to 152(1) pm, consistent with a C-C cluster. C angles of 135.1(6)°, 136.8(6)° and 134.8(6)° with tungsten atoms of the cluster. C-C distances within trifluoroacetate ligands range from 149(1) to 152(1) pm, consistent with a C-C single bond (148 pm), and C-C-F angles vary from 110.7(9)° to 115.2(12)°.

Crystalline powders of \([TBA]_2[W_6I_8(CF_3COO)_6]\) appear orange and show red-orange phosphorescence when exposed to UV radiation (Fig. 4). The phosphorescence can be considered an intrinsic property of the \([W_6I_8(CF_3COO)_6]\)^{2-} cluster anion, and the relative emission intensities of the crystalline powder continuously increases after milling with a highly reflective (inert) solid such as BaSO\(_4\). The quantum yield (\(\phi_q\)) of \([TBA]_2[W_6I_8(CF_3COO)_6]\) is 4% as a pure microcrystalline powder, and 23% after milling with BaSO\(_4\), as determined in an integrating sphere in air.31 The increase of the luminescence intensity may be understood as a result of increased separation of clusters, which are considered as phosphorescence centers. This is in line with the observation of a considerably higher phosphorescence intensity once \([W_6I_8(CF_3COO)_6]\)^{2-} cluster anions are transferred into solution under inert atmosphere, as will be shown later.

The emission spectrum of microcrystalline \([TBA]_2[W_6I_8(CF_3COO)_6]\) shows a broad emission band at 660 nm (1.88 eV) with a full width at half maximum (FWHM) of 2.48 eV (~3500 cm\(^{-1}\)) when excited with 400 nm (Fig. 5). The excitation spectrum of this emission band shows a maximum at 400 nm with full width at half maximum (FWHM) of 2.48 eV (~20000 cm\(^{-1}\)). A similar behavior is reported for \([TBA]_2[Mo_6I_8(CF_3COO)_6]\), which was prepared as a reference material.12

The large FWHM combined with a large Stokes shift of 1.12 eV (~9000 cm\(^{-1}\)) of \([TBA]_2[W_6I_8(CF_3COO)_6]\) can be related to a charge transfer transition.32 The phosphorescence of both compounds is quenched in the presence of oxygen. Emission spectra of \([TBA]_2[W_6I_8(CF_3COO)_6]\) recorded as a function of the oxygen partial pressure are shown in Fig. 5. The phosphorescence intensity as well as the decay time decrease with increasing oxygen partial pressure. The decay time of \([TBA]_2[W_6I_8(CF_3COO)_6]\) in pure nitrogen is 29.2 µs and in pure oxygen 9.9 µs (see ESI†). As the oxygen partial pressure is changed, the photoluminescence intensity as well as the decay time show reversibility within the limit of error of our measurements.

Because the quantum yield of emission is correlated with the decay time (\(\phi = \tau / \tau_r\), where \(\tau\) is the measured decay time and \(\tau_r\) the decay time for the radiative transition),33 the relative decay time, \(\tau_r\), can be used to predict the relative change of the quantum yield.

Accordingly, the relative quantum yield of \([TBA]_2[W_6I_8(CF_3COO)_6]\) emission in pure oxygen atmosphere drops to 34% of the value obtained in pure nitrogen. A similar behavior is observed for \([TBA]_2[Mo_6I_8(CF_3COO)_6]\), where the relative quantum yield drops to 5%. The bimolecular oxygen-mediated quenching processes have been quantified via Stern–Volmer analysis (see Fig. 6). These results imply that this type of cluster compound could be considered as an oxygen sensor. Moreover, the oxygen mediated quenching of the phosphorescent triplet state could potentially lead to the formation of singlet oxygen, \(O_2(a^3\Delta_g)\) (Fig. 1).

The photophysics of the compounds dissolved in acetonitrile was investigated (Table 2). Both clusters show a redshifted emission spectrum, and the emission spectrum of \([TBA]_2[W_6I_8(CF_3COO)_6]\) is particularly broad and extends into the NIR (see ESI†). Phosphorescence lifetimes were determined at three different oxygen concentrations. From these lifetimes, it is possible to calculate the bimolecular rate constant for quenching of the triplet state by oxygen, \(k_q\). Even though the quenching process is not diffusion-limited, it can be calculated that more than 98% of the triplet states are
quenched by oxygen under aerated conditions ($f_T$, Table 2). This is clearly reflected in the very small phosphorescence quantum yields under these conditions.

In order to check if this quenching process involves energy transfer to ground-state oxygen ($X^3Σ_g^-$), the quantum yields of $O_2(a^1Δ_g)$ formation were determined via the characteristic 1275 nm phosphorescence signal from $O_2(a^1Δ_g)$. Indeed, both clusters ($[W_6I_8(CF_3COO)_6]^{2−}$ and $[Mo_6I_8(CF_3COO)_6]^{2−}$) are efficient $O_2(a^1Δ_g)$ photosensitizers under aerated and oxygenated conditions (Table 2). However, for both clusters the observation that the singlet oxygen quantum yield is lower than the fraction of triplet states quenched by oxygen ($Φ_Δ < f_T$) implies that (1) the triplet quantum yield may be below unity and/or (2) some of the encounter complexes between oxygen and the hexanuclear clusters decay via a non-radiative mechanism instead of energy transfer to make singlet oxygen. Such mechanisms often dominate for photosensitizers with appreciable charge-transfer character.34 An interesting direction for future studies could therefore be to systematically develop $[W_6I_8L_6]^{2−}$ cluster compounds and to investigate the effect of ligand-exchange on the singlet oxygen yields and charge-transfer character in the complexes.34c,d Furthermore, solvent-effects could potentially also tune the excited state properties of the clusters.34e,35

The functionalization of photophysically active clusters by means of deposition, incorporation, and encapsulation is a logical need for further applications.10

### Experimental section

#### Materials and methods

Unless otherwise noted, all reactions were carried out in an argon atmosphere in dried and degassed solvents using Schlenk techniques. All solvents were purchased from Sigma-Aldrich, dried and degassed with an MBraun SPS-800 solvent purification system. Chemicals used were obtained from commercial suppliers and were used without further purification.

#### X-ray crystallographic studies

$Cs_2[W_4I_{14}]$. An orange single-crystal of $Cs_2[W_4I_{14}]$ was measured with a single-crystal X-ray diffractometer (STOE-IPDS II) at 25°C using Mo-Kα ($λ = 0.71073$ Å) radiation. Raw data intensities were corrected for Lorentz factors and polarization by the IPDS software. Absorption effects were corrected by the X-Red/X-Shape program of the STOE software. Crystal structure solutions were performed with direct methods (SHELXS), followed by full-matrix least square structure refinements with SHELXL-2014.36 Results are shown in the ESI†.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository number CSD 429577 for $Cs_2[W_4I_{14}]$.

$[TBA]_2[W_4I_{14}]$. Orange crystalline powders were measured and characterized by X-ray powder diffraction (StadiP, Stoe, Darmstadt, Ge-monochromatic Cu-Kα radiation). The crystal structures were indexed isotypically to $[TBA]_2[Mo_6I_{14}]$37 and refined by global refinement using the WinPlotr (FullProf Suite)38. Final R indices and general parameters are given in the ESI†.

$[TBA]_2[W_6I_8(CF_3COO)_6]$. An orange single-crystal of $[TBA]_2[W_6I_8(CF_3COO)_6]$ was measured with a single-crystal X-ray diffractometer (STOE-IPDS II) at −40°C using Mo-Kα ($λ = 0.71073$ Å) radiation. Absorption effects were corrected by the X-Red/X-Shape program of the STOE software. The crystal structure solution and refinement was performed with direct methods (SHELXS) and least square refinements on F² (SHELXL). Some results are shown in Table 1.

### Table 1 Selected crystallographic data for $[TBA]_2[W_6I_{14}(CF_3COO)_6]$

| Parameter                     | Value                   |
|-------------------------------|-------------------------|
| Empirical formula             | Cs₄H₂₂F₂₃In₂N₂O₁₀₂W₆   |
| Formula weight                | 3281.33                 |
| Crystal system                | P1                      |
| a (Å), b (Å), c (Å)           | 1308.62(4), 1321.46(4), 1335.44(4) |
| α, β, γ                      | 114.963(2)°, 102.910(3)°, 102.138(3)° |
| V (Å³)                        | 1.9157(1)               |
| Z, D₀ (g cm⁻³)               | 1.285                   |
| μ (mm⁻¹)                      | 1476                    |
| F(000)                        | 0.2 × 0.1 × 0.1         |
| T⁰, T⁰₀                        | 0.4031, 0.1180          |
| Number of measured and        | 17 913, 6690            |
| independent reflections       |                         |
| Rint                         | 0.0188                  |
| Rf, Rs                        | 0.0348, 0.0763          |
| Largest diff. peak and hole   | 0.667 and −0.592 Å⁻³    |

Fig. 6 Stern–Volmer plots of the emission integrals as well as the decay times of microcrystalline $[TBA]_2[W_6I_8(CF_3COO)_6]$ and $[TBA]_2[Mo_6I_8(CF_3COO)_6]$ powder as a function of oxygen partial pressures.
Table 2. Photophysical data recorded in acetonitrile under varying oxygen concentrations (τ₂ = triplet lifetime; k₂ = bimolecular quenching constant; fᵥ = fractional triplet state quenched by oxygen; Φₚ = quantum yield of phosphorescence; Φₛ = quantum yield of singlet oxygen formation).

| [TBA]₂[W₆I₈(CF₃COO)₆] | (TBA)₂[M₀₆I₆(CF₃COO)₈] |
|----------------------|----------------------|
| λₑm,max [nm]         | 677 ± 2              |
| [TBA]₂[W₆I₈(CF₃COO)₆] | 675 ± 2              |
| τ₁ [μs]              | 36 ± 1               |
| N₂                   | 300 ± 10             |
| Air                  | 1.08 ± 0.02          |
| O₂                   | 1.84 ± 0.03          |
| k₂ [10⁸ M⁻¹ s⁻¹]     | 3.7 ± 0.1            |
| fᵥ                   | 0.98 ± 0.01          |
| Φₚ                   | 0.23 ± 0.01          |
| O₂                   | 0.38 ± 0.01          |
| air                  | 0.99 ± 0.01          |
| Φₛ                   | 0.015 ± 0.003        |
| Air                  | 0.004 ± 0.001        |
| O₂                   | 0.81 ± 0.06          |
| air                  | 0.84 ± 0.07          |
| O₂                   | 0.81 ± 0.06          |
| Air                  | 0.85 ± 0.07          |

Phosphorescence lifetimes of the tungsten cluster were measured using the same instruments as described above. Excitation was done at either 383 or 419 nm, and the phosphorescence signals were isolated using a 650/40 nm band-pass filter. The bimolecular rate constant for quenching of the cluster triplet state by oxygen, k₂, was calculated using a concentration of oxygen in air-saturated acetonitrile of 2.42 mM.41

Phosphorescence quantum yields of the cluster were measured using a home-built setup that allows for acquisition of emission spectra extending to 880 nm. This setup uses the same fs-laser as described above, but for these measurements the detection unit is an Andor Technology, iStar 320 T, ICCD camera connected to an Andor Technology, Shamrock 303i, spectrograph. The detection path is positioned at a 90 degrees angle relative to the excitation path. The detection unit has been intensity calibrated. 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran in acetonitrile (Φₚ = 0.44 ± 0.05)42 and absolute ethanol (Φₚ = 0.435 ± 0.022)43 was used as reference standard.

Synthesis of Cs₂[W₆I₁₄] and (TBA)₂[W₆I₁₄]

2W₃I₁₂ + 2CsI → Cs₂[W₆I₁₄] + 6I₂

W₆I₁₂ (1.2 g, 0.58 mmol) was grounded with CsI (150.3 mg, 0.58 mmol) and filled into a silica ampule. This ampule was flame sealed under vacuum and placed in a tube furnace at 550 °C for 24 h. The product was obtained as a brown powder in quantitative yield.

Cs₂[W₆I₁₄] + 2(TBA)I → (TBA)₂[W₆I₁₄] + 2CsI

769 mg (0.24 mmol) Cs₂[W₆I₁₄] were added to a solution of 270 mg (0.73 mmol) (TBA)I in 100 mL CH₂Cl₂/H₂O (1 : 1). After stirring the mixture for 48 h the organic phase was separated and filtered. The solvent was removed and the precipitate was washed three times with distilled water. The orange solid was then again dissolved in DCM and again filtered. After removing the solvent (TBA)₂[W₆I₁₄] was obtained as an orange solid in 79% yield.

Synthesis of (TBA)₂[W₆I₈(CF₃COO)₆]

(TBA)₂[W₆I₁₄] + 6Ag(CF₃COO) → (TBA)₂[W₆I₈(CF₃COO)₆] + 6AgI

(TBA)₂[W₆I₁₄] (150 mg, 0.044 mmol) was diluted in 35 mL dried DCM and Ag(CF₃COO) (68.9 mg, 0.312 mmol) was added. The reaction was stirred for 72 h in the dark. After filtration the solvent was removed and the brown solid was dissolved in 10 mL of cold ethanol and filtered again. Afterwards the solution was refluxed for 2 h to agglomerate the silver nanoparticles and again filtered. The solvent was then removed in vacuo and the product (TBA)₂[W₆I₈(CF₃COO)₆] was obtained as a yellow powder in 69% yield. To obtain single crystals suitable for X-ray diffraction a saturated solution of the compound in ethanol was over layered with n-pentane and

Crystallographic data (including structure factors) for (TBA)₂[W₆I₁₄] and (TBA)₂[W₆I₈(CF₃COO)₆] has been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB12EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC 1063061 for (TBA)₂[W₆I₁₄] and CCDC 1479582 for (TBA)₂[W₆I₈(CF₃COO)₆].

Solid state photoluminescence measurements

Emission spectra and decay curves were collected with a fluorescence spectrometer FLS920 (Edinburgh Instruments) equipped with a 450 W ozone-free xenon arc lamp (OSRAM) for the emission scan and a μP920H flash lamp for the decay curve. The sample chamber was installed with a mirror optic for the emission scan and a µF920H flash lamp for the decay curve. The sample was in a gas flow sample holder under ambient pressure (about 1 bar) and was perfused with nitrogen, air, oxygen and oxygen–nitrogen mixtures 50/50 and 75/25.

Solution phase spectroscopy

The compounds were dissolved in HPLC-grade acetonitrile (Sigma-Aldrich). Solutions were saturated with N₂ or O₂ by bubbling with the respective gas for at least 30 min. Phenalenone and 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (Sigma-Aldrich) was used as received. All experiments were performed in 1 cm quartz cuvettes.

Equipment and methods used to determine singlet oxygen quantum yields, Φₛ, have been described in detail elsewhere.79 In short, the chromophores were excited using fs-laser pulses centered at 383 nm, and photosensitization of O₂(a¹Δg) was followed via the characteristic phosphorescence signal at ~1275 nm. This signal was isolated using a 1064 nm long-pass filter combined with a 1290/80 nm band-pass filter in front of a VIS/NIR-sensitive PMT. Phenalenone dissolved in acetonitrile was used as the reference sensitizer (Φₛ = 0.99 ± 0.03).40
stored at 3.5 °C. The compound remains stable in moist air, as could be shown by unchanged XRD patterns and unchanged luminescence properties after being exposed to air for several months.

ESI-MS: m/z = 3037.6 ([TBA][W6I4(CF3COO)5]2+; m/z = 2682.5 ([W6I6(CF3COO)4]2–

**Conclusions**

([TBA])2[W6I4(CF3COO)5]2+ represents the first tungsten iodide cluster compound of a growing family of ligand substituted tungsten iodide clusters containing [W6I4L6]2– ions that are currently developed in Tübingen. The present compound exhibits remarkable stability in moist air. Recorded photophysical properties parallel those obtained for parent molybdenum bits remarkable stability in moist air. Recorded photophysical currently developed in Tübingen. The present compound exhibits remarkable stability in moist air. Recorded photophysical properties parallel those obtained for parent molybdenum clusters, represented by a red phosphorescence in solid state and in solution. The phosphorescence emission intensity is quenched with increasing concentration of molecular oxygen, with the formation of singlet oxygen in high yield.

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