$(W_6I_8)Cl_4$ – A Basic Model Compound for Photophysically Active $[(W_6I_8)L_6]^{2-}$ Clusters?

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Abstract. The heteroleptic cluster compound $(W_6I_8)Cl_4$ was prepared by thermal conversion of the homoleptic clusters W_6I_{12} and W_6Cl_{12} at 700 °C to yield a bright yellow powder. The presence of the smaller chlorido ligands in apical positions of $[(W_6I_8)Cl_6]^{2-}$ creates nearly

Introduction

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 M_6X_{12} compounds with M = Mo, W and X = Cl, Br, I are well known.^[6–10] Their structures are based on the octahedral $[M_6X_8^i]$ cluster core containing eight inner (μ_3) and six outer halide ligands, of which four are shared between adjacent clusters (i = *innen* or *inner*, a = $au\beta en$ or *outer*) according to notation $[(M_6X_8^i)X_2^aX_{4/2}^{a-a}].$

Many clusters of this type behave chemically stable under various conditions and it is clear that the apical (outer) ligands are more loosely bound to the cluster core, thus allowing for a manifold of exchange reactions with various inorganic or organic ligands.^[1]

Photophysical studies on homoleptic and heteroleptic $[W_6X_8{}^iX_6{}^a]^{2-}$ cluster compounds (in which X^i and X^a are Cl, Br, I) have revealed that the all iodide cluster shows the highest luminescence intensity ($\varphi_{em} = 0.39$) and the most blue shifted emission band (at 698 nm for (TBA)₂[W₆X₈ⁱX₆^a]) in aceto-nitrile.^[2]

Compounds with the octahedral molybdenum halide cluster $[Mo_6I_8L_6]^{2-}$, in which L is an inorganic or organic ligand have received great attention due to their remarkable photophysical and photochemical properties.^[3] These compounds exhibit photoluminescence properties with typical emissions in the red to infra-red region, and excellent potential in the generation of singlet oxygen, in solid state and in solution.

The importance of $[Mo_6I_8L_6]^{2-}$ photosensitizers inspired us to create corresponding $[(W_6I_8)L_6]^{2-}$ clusters, which are currently developed.^[4] In these compounds, terminal ligands play

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University of Applied Sciences Münster Stegerwaldstrasse 39 48565 Steinfurt, Germany spherically clusters showing thermal and chemical inertness. Photoluminescence studies revealed a strong red phosphorescence from excited spin-triplet states.

a crucial role regarding properties. This prompted us to develop the basic heteroleptic cluster compound $(W_6I_8)Cl_4$ as a prototype compound for $[M_6I_8L_6]^{2-}$ photosensitizers, which is reported herein.

Results and Discussion

Synthesis and Structure

Syntheses of homoleptic M_6X_{12} (M = Mo, W; X = Cl, Br, I) cluster compounds have been described based on several different procedures given in the literature.^[5] For the preparation of the new heteroleptic cluster compound (W_6I_8)Cl₄ we use an unconventional but simple solid-state reaction between W_6I_{12} and W_6Cl_{12} . This reaction takes advantage of the higher thermal stability of W_6I_{12} compared to W_6Cl_{12} . W_6I_{12} can be treated at 700 °C in a sealed quartz tube without decomposition, whereas W_6Cl_{12} has been shown to decompose into the elements near 550 °C when treated under similar conditions. When W_6I_{12} and W_6Cl_{12} were reacted, the formation of some elemental tungsten as side-phase was inevitable, which introduced a light greying to the observed (W_6I_8)Cl₄ powder.

 $(W_6I_8)Cl_4$ was obtained as an orange-yellow crystalline powder containing plate-like single-crystals, which were used for structure determination and refinement by means of X-ray diffraction. The substitution of the apical iodido ligands in W_6I_{12} by chlorido ligands in the heteroleptic $(W_6I_8)Cl_4$ involves a change of the color from brown to bright yellow (Figure 1), which is related to the *canary yellow* color of W_6Cl_{12} .

The crystal structure of $(W_6I_8)Cl_4$ refined with the space group *Cmca* (Table 1 and Table 2), is closely related to the structure of W_6X_{12} (X = Cl, Br, I). The cluster connectivity of $[(W_6I_8^i)Cl_2^aCl_{4/2}^{a-a}]$ is represented by four inter-cluster-bridging chlorido ligands (Cl^{a-a}) forming the characteristic two-dimensional layer structure of W_6X_{12} compounds, as displayed in Figure 2. The octahedral [W₆] cluster core contains W–W distances within the range 265.04(7)–265.23(7) pm, with an average value of 265.11(6) pm. W–I contacts with (inner) face-

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Figure 1. Optical photographs of crystalline powders (top row) of W_6I_{12} starting material (left), $(W_6I_8)Cl_4$ under daylight (middle), and (W₆I₈)Cl₄ under 366 nm excitation (right). A crystal of (W₆I₈)Cl₄ is shown below under daylight and under 366 nm excitation (bottom row).

capping iodido ligands range within 278.62(6)-280.34(6) pm, with an average value of 279.37(6) pm. Six chlorido ligands are situated in (outer) apical positions of the cluster. Four of them generate a bridging connectivity with W-Cl distances of 253.6(3) pm (Figure 2). Another two apical chlorido ligands appear as terminal ligands with W-Cl distances at 246.2(3) pm. All in all, the crystal structure of $(W_6I_8)Cl_4$ corresponds to the structure of its homoleptic $W_6 X_{12}$ counterparts, best described by the [(W₆I₈ⁱ)Cl₂^aCl_{4/2}^{a-a}] connectivity.

Table 1. Crystal data and structure refinement data for (W₆I₈)Cl₄.

	$(W_6I_8)Cl_4$
Formula weight	2260.10
Temperature /K	293(2)
Wavelength /nm	71 073
Crystal system	orthorhombic
Space group	Cmca (no. 64)
Unit cell dimensions	emea (net et)
a /pm	1560.6(2)
<i>b</i> /pm	1209.5(2)
c /pm	1210.5(2)
Volume /nm ³	2.2848(6)
Z	4
Density (calculated) $/g \cdot cm^{-3}$	6.570
Absorption coefficient /mm ⁻¹	41.343
F(000)	3744
Crystal size /mm ³	$0.12 \times 0.1 \times 0.007$
Theta range for data collection /°	3.366 to 25.327
Index ranges	$-18 \le h \le 18$
	$-14 \le k \le 14$
	$-14 \le l \le 14$
Reflections collected	10388
Independent reflections	1083
<i>R</i> (int)	0.0173
Completeness to $\theta = 25.242^{\circ}$	98.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1083 / 0 / 47
Goodness-of-fit on F ²	1.159
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0212, wR_2 = 0.0552$
R indices (all data)	$R_1 = 0.0217, wR_2 = 0.0554$
Largest diff. peak and hole $/e \cdot Å^{-3}$	3.132 and -1.335

Interatomic distances in (W₆I₈)Cl₄ can be well related with corresponding distances obtained in similar W₆X₁₂ cluster

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (pm² × 10⁻¹) for (W₆I₈)Cl₄. U_{eq} is defined as one third of the trace of the orthogonalized U_{ii} tensor.

Atom	x	у	z	$U_{ m eq}$
W(1)	0.1201(1)	0	1/2	13(1)
W(2)	0	0.0851(1)	0.6295(1)	13(1)
W(3)	0	0.1296(1)	0.4151(1)	13(1)
I(1)	0.1253(1)	0.0472(1)	0.2733(1)	25(1)
I(2)	0.1259(1)	0.2267(1)	0.5473(1)	25(1)
Cl(1)	0.2778(2)	0	1/2	26(1)
Cl(2)	0	0.3122(3)	0.3121(3)	33(1)



Figure 2. Two-dimensional projection of a section of the crystal structure of [(W₆I₈ⁱ)Cl_{4/2}^{a-a}Cl₂^a] (color code: W blue, I violet, and Cl green).

compounds, which are summarized in Table 3. A major difference to corresponding compounds of this type is the enlargement of W-Cl-W angles (148.8°), due to the smaller chlorido ligands in (W₆I₈)Cl₄. The smaller chlorido ligands in apical positions of the $[(W_6I_8)Cl_6]^{2-}$ fragment in Figure 3 make up for a nearly spherical cluster moiety, having a diameter in the order of 100 nm.

Outer ligands of $[(M_6X_8^i)X_6^a]^{2-}$ clusters (M = Mo, W) are usually more loosely bound to the cluster core, which may be due also to the repulsion with inner X ligands (matrix effect), provoking that outer ligands have relatively long M-X distances, and can be more easily removed or substituted. With the presence of the smaller chlorido ligands in apical positions of the $[(W_6I_8)Cl_6]^{2-}$ cluster this repulsion may be reduced, as we note significantly short M-X distances for W-Cla and W-Cl^{a-a} in $(W_6I_8)Cl_4$ (Table 3). $(W_6I_8)Cl_4$ appears as a thermally and chemically stable material. According to a thermal treatment in an evacuated silica tube (W₆I₈)Cl₄ is thermally stable up to 750 °C. In air it behaves stable up to 250 °C according to DTA (differential thermal analysis) measurements. (W₆I₈)Cl₄ is chemically inert in the presence of concentrated acids (HCl, HF, HNO₃, or H₂SO₄) and stable in strong alkaline solutions.

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	Mo ₆ Cl ₁₂ ^[6]	Mo ₆ Br ₁₂ ^[7]	Mo ₆ I ₁₂ ^[8]	W ₆ Br ₁₂ ^[9]	$(W_6I_8)Cl_4$	$W_6 I_{12}^{[10]}$	
M–M	260.63(7)	263.1(1)	267.2(4)	263(2)	265.11(6)	266.5(3)	
$M-X^{i}$	247.0(1)	259.7(1)	2.773(3)	262(4)	279.37(6)	279.5(6)	
$M - X^{a-a}$	249.3(2)	265.3(2)	289.1(5)	265(5)	253.6(3)	288.9(4)	
$M-X^{a}$	238.0(2)	255.1(2)	2.805(5)	250(3)	246.2(3)	279.7(5)	
M-I-M	131.18(6)	131.76(7)	133.5(2)	132.0(2)	148.76(1)	134.3(2)	
V	1785.2(8)	2048.8(3)	2494(1)	2061.5(3)	2284.8(6)	2508(1)	

Table 3. Comparison of distances /pm, selected angles /°, and unit cell volumes $V/Å^3$ in M_6X_{12} compounds with M = Mo, W.



Figure 3. Space filling structure drawing of an isolated $[(W_6I_8)Cl_6]^{2-}$ fragment (left) contained in the $(W_6I_8)Cl_4$ structure and a corresponding drawing, in which atoms are shown as contracted spheres, interconnected with lines that characterize interatomic bonds (right).

Photoluminescence

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First photophysical studies on Mo_6Cl_{12} were reported several years ago, showing that molybdenum halide clusters are strongly photoluminescent.^[12] M_6Cl_{12} compounds containing the $[(M_6Cl_8)Cl_6]^{2-}$ ion (M = Mo, W) show red luminescence in solid state under UV/Vis photoexcitation.^[15] When dissolved in organic solvents, the photoluminescence of $[(Mo_6Cl_8)Cl_6]^{2-}$ cluster ions is increasingly quenched with the amount of molecular oxygen in solution.^[11] Alongside with a rather long luminescence emission lifetime and other experimental evidence, the excited state properties were interpreted as phosphorescence emission from excited spin-triplet states. The temperature dependence of the emission and of the decay time of $[(Mo_6Cl_8)Cl_6]^{2-}$ cluster anions were explained by the emission from the three excited triplet-state sublevels.^[12]

Solid (W_6I_8)Cl₄ shows a broad absorption band in the range between 250 and 550 nm, displayed in Figure 4. Upon excitation at 450 nm there appears a very broad emission band peaking at 635 nm (1.95 eV) with a FWHM of 110 nm (0.33 eV), with a decay time of about 57 μ s.

Temperature dependent emission spectra are obtained upon 450 nm excitation. The emission intensity of $(W_6I_8)CI_4$ is low at room temperature, as can be estimated from the emission spectra in Figure 5, which may be caused be concentration quenching of adjacent clusters in crystal grains. Expectedly, the intensity increases with decreasing temperature. Usually, the temperature dependency of the position of the emission maximum is a result of the redistribution of excited triplet spin-states. For $(W_6I_8)CI_4$ we monitored a peculiar temperature dependency, shown in Figure 5. The emission maximum shows a red-shift between 100 to 200 K and then a blue-shift from 200 to 500 K. The red-shift behavior of the emission maximum is due to emission bands originating from several excited spin-triplet state sublevels, whereby the occupation of these energy levels varies with temperature.



Figure 4. Excitation spectrum of (W₆I₈)Cl₄ monitored at 650 nm.



Figure 5. Emission spectra of $(W_6I_8)Cl_4$ between 100 and 500 K upon 450 nm excitation.

A similar behavior of emission bands was studied in much detail, where spectral fitting procedures have resulted in three triplet states for $[Mo_6Cl_{14}]^{2-}$ and four triplet states for $[Re_6S_8X_6]^{4-}$ ($X = Cl^-$, Br^- , I^-).^[13]

Different oxygen partial pressures showed no influence on the luminescence intensity of solid $(W_6I_8)Cl_4$. This give raise to the assumption that $(W_6I_8)Cl_4$ is not efficient in the generation of singlet oxygen. The same was demonstrated for solid $(TBA)_2[W_6I_{14}]$.^[4] Oxygen quenching is only apparent once $[W_6I_{14}]^{2-}$ clusters are dissolved into solution (e.g. in acetonitrile, acetone, alcohol), and a strongly enhanced photophysical activity with respect to luminescence intensity or singlet oxygen production is obtained for compounds containing $[M_6X_8^{i}L_6^{a}]^{2-}$ ions (M = Mo, W) mentioned in the introduction part.

Moreover, $(TBA)_2[M_6X_8^iL_6^a]$ (M = Mo, W) exhibits strong luminescence quenching in the presence of molecular oxygen in solid state.^[3,4] in contrast to what is obtained for $(W_6I_8)Cl_4$.

Conclusions

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The new compound $(W_6I_8)Cl_4$ appears as a crystalline yellow to orange powder. The crystal structure was characterized by single-crystal XRD techniques and the photoluminescence behavior was studied. $(W_6I_8)Cl_4$ reveals a broad excitation in the UV/Vis range and shows a red emission at low temperatures. Compared to ligand substituted $[Mo_6I_8L_6]^{2-}$ clusters there is no significant luminescence quenching of $(W_6I_8)Cl_4$ by molecular oxygen in solid state.

Experimental Section

X-ray Crystallographic Study of (W₆I₈)Cl₄: An orange single-crystal of (W₆I₈)Cl₄ was measured with a single-crystal X-ray diffractometer (STOE-IPDS) at room temperature (T = 293 K) using Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The crystal structure refinement and solution was performed with direct methods (SHELXS) and least square refinements on F^2 (SHELXL14^[14]).

Some results and final R values are shown in Table 1, atom positions are given in Table 2, and some selected distances are collected in Table 3.

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-429579.

Reaction products were inspected by powder X-ray diffraction with a Stadi-P (STOE, Darmstadt) diffractometer with germanium monochromated Cu- $K_{\alpha 1}$ radiation.

Photoluminescence Measurements: Excitation and emission spectra as well as decay curves were collected with a fluorescence spectrometer FLS920 (Edinburgh Instruments) equipped with a 450 W ozone free xenon arc lamp (OSRAM) and a sample chamber installed with a mirror optic for powder samples. For detection, a R2658P single-photon counting photomultiplier tube (Hamamatsu) was used. All luminescence spectra were recorded with a spectral resolution of 1 nm, a dwell time of 0.4 s in 1 nm steps, and three repeats. Reflection spectra were monitored by placing the sample into an integrating sphere coated with spectralon and using a synchronous scan, i.e., the excitation and emission monochromator were adjusted to the same wavelength and tuned synchronously. These reflection spectra were recorded with an Edinburgh Instruments FS900 spectrometer equipped with a 450 W Xe arc lamp and cooled single-photon counting photomultiplier (Hamamatsu R928). BaSO₄ (99%, Sigma-Aldrich) was used as a reflectance standard.

Synthesis of (W₆I₈)Cl₄

$$W_6Cl_{12} + 2W_6I_{12} \rightarrow 3[W_6I_8]Cl_4$$

 $W_6Cl_{12} \rightarrow 6W + 6Cl_2$ (side reaction)

(2)

A mixture of 1:2 molar ratio of $W_6Cl_{12}^{[15]}$ (0.033 mmol, 50 mg) and $W_6I_{12}^{[10,16]}$ (0.066 mmol, 172 mg) was ground in a mortar and charged into a silica tube. The ampoule was flame-sealed under vacuum. The mixture was heated for 12 h at 600 °C with a heating and cooling rate of 2 K·min⁻¹. (W₆I₈)Cl₄ was obtained as a yellow-orange powder in 60% yield [Equation (1)] with elementary tungsten as a side-phase [Equation (2)].

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