Photoluminescence of Antimony(III) and Bismuth(III) Chloride Complexes in Solution

Hans Nikol and Arnd Vogler

Institut für Anorganische Chemie
Universität Regensburg, Universitätstrasse 31
D-8400 Regensburg, Federal Republic of Germany

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Metal-centered (MC) excited states play an important role in the photophysics and photochemistry of coordination compounds. However, the study of MC states has been essentially limited to d and f block elements, while the main group metal systems are largely ignored. This lack of knowledge is quite surprising since MC excited states of many main group metal complexes can be easily studied by emission spectroscopy under ambient conditions. Although simple halide complexes of s-block metals such as Ti⁺, Sn²⁺, Pb⁺, and Sb⁺⁺ are known to be luminescent in solution, this observation has been occasionally used only for analytical applications but hardly for the characterization of the emitting excited state. On the contrary, the emission of s⁻ ions which are doped into host lattices has been studied in detail by solid-state physicists. We report here our observations on the photoluminescence of SbCl₄⁻, Sb₂Cl₆⁻, BiCl₄⁻, and Bi₂Cl₆⁻ in solution and discuss the nature of the emitting excited state. While an emission of SbCl₄⁻ in CHCl₃ has been reported before, the other three complex ions are not yet known to show photoluminescence in solution at room temperature.

The compounds [NEt₄]SbCl₄ and [NEt₄]BiCl₄ were prepared according to published procedures. The complex ions SbCl₄⁻ and BiCl₄⁻ in acetonitrile were formed by the addition of an excess of [NEt₄]Cl to the MC¹⁺ ions. The absorption spectrum of SbCl₄⁻ in acetonitrile (Figure 1) displays three bands (Table I). Light absorption by SbCl₄⁻ was accompanied by a red emission (Figure 1, Table I). The excitation spectrum agreed well with the absorption spectrum. Upon addition of chloride SbCl₃Cl⁻ was converted to SbCl₂⁻ which has an absorption spectrum (Figure 1, Table I) similar to that of SbCl₄⁻. Light absorption by SbCl₂⁻ led to a green emission (Figure 1, Table I). Again, the excitation spectrum matched the absorption spectrum. If light absorption was complete (A > 2), the progressive conversion of SbCl₄⁻ to SbCl₂⁻ was accompanied by the appearance of an isoemissive point at λ = 613 nm. The absorption and emission spectra of BiCl₄⁻ and Bi₂Cl₆⁻ (Figure 2) showed features (Table I) which are analogous to those of SbCl₂⁻ and SbCl₄⁻. In contrast to the antimony complexes, the B band of the bismuth compounds was not observed in accordance with results on Cs₂NaYCl₆ doped with Bi⁺⁺.

According to the VSEPR model the structures of complexes of s-block metal ions should be determined by the presence of a stereochemically active lone pair. However, s⁻ complexes with a coordination number of six are generally octahedral, and thus they are exceptions from the rule. This applies also to the structures

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Supplementary Material Available: Tables listing atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for I and 3, and an ORTEP plot for Li(TMEDA)₄; (15 pages); tables of observed and calculated structure factors for 1 and 3 (21 pages). Ordering information is given on any current masthead page.


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Table 1. Absorption and Emission Spectra of MCl₄⁻ and MCl₆⁻ (M = Sb, Bi) in CH₃CN at Room Temperature

<table>
<thead>
<tr>
<th></th>
<th>SbCl₄⁻</th>
<th>SbCl₆⁻</th>
<th>BiCl₄⁻</th>
<th>BiCl₆⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>absorption, λ_max [nm]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(e [1 mol⁻¹ cm⁻¹])</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A band</td>
<td>283</td>
<td>306</td>
<td>319</td>
<td>333</td>
</tr>
<tr>
<td></td>
<td>(1600)</td>
<td>(1600)</td>
<td>(5100)</td>
<td>(10300)</td>
</tr>
<tr>
<td>B band</td>
<td>255</td>
<td>267</td>
<td>242</td>
<td>227</td>
</tr>
<tr>
<td></td>
<td>(3500)</td>
<td>(5000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C band</td>
<td>235</td>
<td>242</td>
<td>227</td>
<td>231</td>
</tr>
<tr>
<td></td>
<td>(5000)</td>
<td>(13300)</td>
<td>(12300)</td>
<td>(36000)</td>
</tr>
<tr>
<td>emission, λ_max [nm]</td>
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<td>520</td>
<td>720</td>
<td>475</td>
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<tr>
<td>φ [×10⁴]</td>
<td>6.1</td>
<td>1.3</td>
<td>10.0</td>
<td>4.0</td>
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<tr>
<td>stokes shift [cm⁻¹]</td>
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<td>13500</td>
<td>17500</td>
<td>9000</td>
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</tbody>
</table>

Figure 1. Electronic absorption (left side) and emission (right side) spectra of [NEt₄]SbCl₄ in acetonitrile at room temperature, 1-cm cell. Absorption: 2.54 × 10⁻⁴ M (a) and in the presence of 0.1 M [NEt₄]Cl (b). Emission: 5.0 × 10⁻⁴ M (a) and in the presence of 0.008, 0.01, 0.02, 0.04, 0.06, and 0.08 M [NEt₄]Cl (g). λ_max = 290 nm, intensity in arbitrary units.

Figure 2. Electronic absorption (left side) and emission (right side) spectra of [NEt₄]BiCl₄ in acetonitrile at room temperature, 1-cm cell. Absorption: 1.08 × 10⁻⁴ M (a) and in the presence of 0.05 M [NEt₄]Cl (b). Emission: 4.0 × 10⁻⁴ M (a) and in the presence of 0.033 M [NEt₄]Cl (b). λ_max = 313 nm, intensity in arbitrary units.

of SbCl₄⁻, SbCl₆⁻, and BiCl₄⁻, which are octahedral. The absorption spectra of both complexes are characterized by MC s → p transitions from the HOMO a* to the LUMO t*₁. This transition gives rise to three absorption bands (Table 1) which originate from the transitions of the free s² ions: ¹S₀ → ³P₁ (A band), ¹P₂ (B), ³P₁ (C) and in the presence of 0.1 M [NEt₄]Cl (b). Emission: 5.0 × 10⁻⁴ M (a) and in the presence of 0.008, 0.01, 0.02, 0.04, 0.06, and 0.08 M [NEt₄]Cl (g). λ_max = 290 nm, intensity in arbitrary units.

(11) Complex ions of s² metals may adopt a variety of coordination numbers and geometries. In the solid state the structures can be modified by the counter ion. Nevertheless, at a coordination number of six the complexes are octahedral or nearly so.

Figure 3. Qualitative MO scheme of MCl₄⁻ (M = Sb, Bi) in T₅ and C₂ᵥ (butterfly structure) symmetry; σ orbitals of the ligands are omitted.

(butterfly structure) symmetry; σ orbitals of the ligands are omitted. 

(15) In the solid-state polymeric structures which are associated with an expansion of the coordination number are frequently formed.
(18) Numerous structures of MX₄ salts with M = Sb, Bi and X = halide, pseudohalide have been determined by X-ray analysis. Generally, polymeric structures with variable coordination numbers have been found. However, it was shown that in many solids with varying metal–ligand distances MX₄ moieties with a butterfly structure can be recognized.
We suggest that the ground-state distortion of $\text{MCl}_4^-$ is eliminated in the excited state. The stabilization of the $\text{C}_2$ butterfly structure is essentially lost in the $a_1^*, b_1^* \rightarrow b_1^*, a_2^*, b_2^*$ sp excited state (Figure 3) which rearranges toward a symmetrical tetrahedral geometry. This structural change now explains easily the immense Stokes shift of $\text{MCl}_4^-$. An analogous approach has been used before in solid-state physics. Blasse and his group have shown that $s^2$ ions which are doped into host lattices may also show large Stokes shifts if the structure is essentially lost in the all-hedral geometry. This structural change now explains easily the

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**The Return of the Trapped Electron in X-Irradiated Clathrate Hydrates. An ESR Investigation**

Janusz Bednarek,* Roland Erickson,† Anders Lund,* and Shulamith Schlick*§

*Department of Chemistry, University of Detroit
Detroit, Michigan 48221

†Department of Physics, Linkping University
S-581 83 Linkoping, Sweden

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The search of an ideal host for the formation and detection of trapped electrons in organic single crystals has lead us to a large family of clathrate hydrates containing peralkylammonium hydroxide guests. The presence of trapped electrons has been detected by pulse radiolysis at room temperature in a large number of the clathrates.1,2

Two compounds were chosen for this initial study of electron stabilization: tetramethylammonium hydroxide pentahydrate, (CH$_3$)$_4$N$^+$OH$^{-}$5H$_2$O, mp 335 K (TMNOH, I), and tetra-n-butylammonium hydroxide hydrate, (C$_4$H$_9$)$_4$N$^+$OH$^{-}$3H$_2$O, mp 303 K (TBNOH, II). This selection was made because the crystal structure for both hydrates has been determined,3-4 the melting points are above ambient temperature, and because the amount of water in the stoichiometric compounds is large, about 50% by weight in I and 68% in II; therefore, the radiolytic behavior of these hydrates can be compared to the well-known results for other forms of water (ice, liquid, and glass).

Compound II has the typical crystal structure of most peralkylammonium hydrates based on the pentagonal dodecahedral unit. Compound I is unique among the peralkylammonium hydrates, in that its structure is based on a truncated octahedron and is shown in Figure 1.4,5 The distances between the nitrogen (N) in the center and the oxygen atoms of the cage range from 4.30 (to O1) to 4.97 Å (to O2), and the average is 4.61 ± 0.16 Å.

Exciting results have been reported recently on some clathrates, using $^{125}$Xe NMR6 and gas-phase mass spectroscopic techniques.7

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*Author to whom correspondence should be addressed.

1On leave from the Institute of Applied Radiation Chemistry, Technical University, Lodz, Poland.

2University of Detroit.

3Linkoping University.

