Photoluminescence of Germanium(II), Tin(II), and Lead(II) Chloride Complexes in Solution

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Received March 13, 1992

The absorption and emission spectra of GeCl₃⁻, SnCl₃⁻, PbCl₂⁻, and PbCl₄²⁻ in acetonitrile were recorded. In addition, emission quantum yields and lifetimes were determined. The emitting excited states are of the metal-centered sp type and originate from the 3P state of the free s⁺ ions. It is suggested that the complex ions which have trigonal-pyramidal C₃v (MCl₃⁻) and seesaw C₂ᵥ (PbCl₂⁻) structures in the ground state rearrange toward trigonal-planar D₃h and tetrahedral T₄g geometries, respectively, in their sp excited states.

Introduction

Emission spectroscopy is of overwhelming importance in the field of photophysics and photochemistry. With regard to coordination compounds, the application of this technique has been essentially restricted to transition metals, while very little is known about the luminescence of main group metal complexes. A systematic investigation of the emission spectra of such complexes in solution first results were obtained with the anions MCl⁻ and MCl₂⁻ (M = Sn²⁺, Bi³⁺). The present study, which deals with the complexes MCl₃⁻ and MCl₄⁻ of the group IV metal ions Ge²⁺, Sn²⁺, and Pb²⁺, is a significant extension of this work. Sn²⁺ and Pb²⁺ have attracted much attention in recent years. ¹¹⁻² Due to the high coordinating ability of acetonitrile, well-defined chloro complexes of Ge²⁺, Sn²⁺, and Pb²⁺ are formed in this solvent.

Not only is the present investigation interesting in its own right, but our observations are also important for other areas. Since MCl₃⁻ (M = Ge, Sn, Pb) is isoelectronic with carbanions C₃⁻, our findings may be related to the yet unknown excited states of these organic intermediates. Furthermore, the intriguing emission behavior of the homonuclear Sn₂⁺ cluster compound [Sn₄O₆(OCH₃)₂]₄⁻ and polynuclear metal complexes which contain a bond between a transition metal and Ge²⁺, Sn²⁺, and Pb²⁺ has attracted much attention in recent years. ¹¹⁻¹² Accordingly, the study of simple complexes of these M²⁺ ions should be of great value for the understanding of the more complicated polynuclear complexes. Finally, it should be mentioned that there is a remarkable photochemistry of chloro complexes of Sn²⁺,¹³⁻¹⁵ The photooxidation of Sn²⁺ can be applied for electroless metal deposition in the electronics industry.¹⁴ The present investigation serves also to characterize the reactive excited states which were not identified in previous studies.

Experimental Section

Materials. [NEt₄]GeCl₃ and [NEt₄]SnCl₃ were prepared according to a published procedure.¹⁶ [NEt₄]PbCl₂ was synthesized by a procedure similar to that of the preparation of [NH₄]PbCl₃.¹⁷ Acetonitrile was spectrograde.

Spectroscopy. Absorption spectra were measured with an Uvikon 860 double-beam spectrophotometer. Emission spectra were obtained on a Hitachi 850 spectrofluorimeter which was equipped with a Hamamatsu 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency. Absolute emission quantum yields were determined by comparison of integrated emission intensity of GeCl₃⁻, SnCl₃⁻, PbCl₂⁻, and PbCl₄²⁻ with that of quinine sulfate in 0.5 M H₂SO₄ (λmax = 452 nm; φ = 0.546) at identical conditions such as exciting wavelength, optical density, and apparatus parameters.

Results

The absorption spectra of the complex ions MCl_n⁻ in CH₃CN were characterized by UV bands (Figures 1–3, Table 1). Upon addition of chloride to solutions of GeCl₃⁻ and SnCl₃⁻ in CH₃CN, the absorption spectra did not change. In typical experiments, the complex concentrations were approximately 10⁻⁴ M and chloride was added up to 0.5 M. It follows that Ge²⁺ and Sn²⁺ do not form complexes MClₙ⁻ with n ≥ 3 under these conditions. On the contrary, the addition of Cl⁻ to solutions of PbCl₄²⁻ was accompanied by spectral variations, including clear isosbestic points at 284 and 255 nm (Figure 3). Finally, the original band was completely replaced by the new absorption. According to an analysis of the spectral changes and their dependency on the concentration of added chloride, the new band at λmax = 294 nm was attributed to PbCl₄²⁻ (Table 1). The absorption and emission spectra of GeCl₃⁻, SnCl₃⁻, PbCl₂⁻, and PbCl₄²⁻ in acetonitrile were recorded. In addition, emission quantum yields and lifetimes were determined. The emitting excited states are of the metal-centered sp type and originate from the 3P state of the free s⁺ ions. It is suggested that the complex ions which have trigonal-pyramidal C₃v (MCl₃⁻) and seesaw C₂ᵥ (PbCl₂⁻) structures in the ground state rearrange toward trigonal-planar D₃h and tetrahedral T₄g geometries, respectively, in their sp excited states.
apparently hampered by their photochemical instability. In de-

Figure 1. Electronic absorption (left side) and emission (right side) spectra of 
[NEt4][GeCl3] in acetonitrile at room temperature (1-cm cell). Absorption: 1.94 \times 10^{-4} M. Emission: 7.43 \times 10^{-4} M, \lambda_{ex} = 250 nm, intensity in arbitrary units.

librium constant \( \left[ \text{PbCl}_3^- + \text{Cl}^- \right] \) was rather small \( (K = 8.5 \times 10^{-2} \text{ L mol}^{-1}) \). Upon light absorption, all four complex ions in \( \text{CH}_3\text{CN} \) showed a green luminescence at room temperature (Figures 1–3, Table I). The excitation spectra matched the absorption spectra rather well. The emission lifetimes could be determined only for \( \text{PbCl}_3^- \) and \( \text{PbCl}_4^{2-} \), while \( \text{GeCl}_3^- \) and \( \text{SnCl}_3^- \) did not yield reproducible results. The lifetime measurements of the latter ions were apparently hampered by their photochemical instability. In de-aerated solutions the luminescence was rather intense. In the presence of oxygen, the emission intensity was much lower (Table I).

Figure 2. Electronic absorption (left side) and emission (right side) spectra of 
[NEt4][SnCl3] in acetonitrile at room temperature (1-cm cell). Absorption: 6.0 \times 10^{-5} M. Emission: 7.0 \times 10^{-4} M, \lambda_{ex} = 250 nm, intensity in arbitrary units.

Figure 3. Electronic absorption (left side) and emission (right side) spectra of 
[NEt4][PbCl3] in acetonitrile at room temperature (1-cm cell). Absorption: 1.8 \times 10^{-4} M without [NEt4]Cl (a) and in the presence of 0.016, 0.043, 0.066, 0.124, and 0.240 M [NEt4]Cl (f). Emission: 2.25 \times 10^{-4} M without [NH4]Cl (a) and in the presence of 1 M [NEt4]Cl (f), \lambda_{ex} = 250 nm, intensity in arbitrary units.

Discussion

The electronic spectra of \( s^2 \) ions doped into solid matrices such as halides and oxides have been investigated extensively.\(^{(19,20)}\) In all cases, the basic pattern of the absorption spectra is quite similar. The low-energy bands can be assigned to \( s \rightarrow p \) transitions. An \( s^2 \) ion has a \( 1S_0 \) ground state and \( 3P_0, 3P_1, 3P_2 \), and \( 1P_1 \) \( sp \) excited states. The \( 1S_0 \rightarrow 3P_0 \) transition is strongly forbidden and not observed in absorption. The spectrum is characterized by the \( A \) \( (1S_0 \rightarrow 3P_1) \), \( B \) \( (1S_0 \rightarrow 3P_2) \), and \( C \) \( (1S_0 \rightarrow 1P_1) \) bands with decreasing wavelength. The energy of these transitions depends on the metal and is modified by the matrix, but the essential features of the spectrum do not change.\(^{(19,20)}\) The absorption bands of \( \text{MCl}_3^- \) and \( \text{MCl}_4^{2-} \) in \( \text{CH}_3\text{CN} \) (Table I) were assigned by analogy to the spectra of the \( M^{2+} \) ions in halide matrices.\(^{(19,20)}\) In any case, the longest-wavelength absorption is always the \( A \) band.

Generally, the emission of \( s^2 \) ions in solid matrices originates from the \( 1P_1 \) level.\(^{(19,20)}\) There is little doubt that the luminescence of \( \text{MCl}_3^- \) and \( \text{MCl}_4^{2-} \) (Figures 1–3, Table I) can also be assigned to the \( 1P_1 \rightarrow 1S_0 \) transition. The rather long emission lifetime is in agreement with a spin-forbidden transition. However, considerable singlet–triplet mixing facilitated by the heavy-atom effect of the \( s^2 \) ions does certainly occur.

In summary, the emission and longest-wavelength absorption bands of \( \text{MCl}_3^- \) and \( \text{MCl}_4^{2-} \) can be reliably assigned to a metal-centered transition which involves the \( s \) and \( p \) metal orbitals. However, such a simple model which is based on the electronic transitions of the free ions does not account for other spectral features such as the Stokes shift. The structures of the complex ions in the ground and excited states obviously must be included for a more appropriate description.

According to the VSEPR model developed by Gillespie and Nyholm,\(^{(22)}\) all \( AX_3 \) and \( AX_2 \) molecules or ions with a \( s^2 \) central atom are trigonal-pyramidal (\( C_3 \)) and butterfly (or seesaw) (\( C_2 \)) structured, respectively. The \( \text{MCl}_3^- \) and \( \text{MCl}_4^{2-} \) complexes in acetonitrile certainly also exist as these structures. This assumption is supported by far-infrared and Raman spectral data of solutions of \( \text{GeX}_3^- \) and \( \text{SnX}_3^- \),\(^{(23,24)}\) respectively, and solid-state structures of \( \text{GeCl}_3^- \),\(^{(25-27)}\) \( \text{SnCl}_3^- \),\(^{(25-29)}\) and \( \text{PbCl}_3^- \) as determined.

Table I. Absorption and Emission Data for \( \text{MCl}_3^- \) (\( M = \text{Ge, Sn, Pb} \)) and \( \text{MCl}_4^{2-} \) (\( M = \text{Pb} \)) in \( \text{CH}_3\text{CN} \) at Room Temperature

<table>
<thead>
<tr>
<th>( \text{MCl}_3^- )</th>
<th>( \text{SnCl}_3^- )</th>
<th>( \text{PbCl}_3^- )</th>
<th>( \text{PbCl}_4^{2-} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption ( \lambda_{abs} ) (A band), nm</td>
<td>280</td>
<td>292, 277</td>
<td>273</td>
</tr>
<tr>
<td>( (s, \text{L mol}^{-1} \text{cm}^{-1}) )</td>
<td>(30)</td>
<td>(300, 700)</td>
<td>(8100)</td>
</tr>
<tr>
<td>Absorption ( \lambda_{bands} ) (C band), nm</td>
<td>218, 225</td>
<td>216, 226, 236</td>
<td>205</td>
</tr>
<tr>
<td>( (10^{-4}, \text{L mol}^{-1} \text{cm}^{-1}) )</td>
<td>(4.9, 4.8)</td>
<td>(12.9, 17.3, 14.0)</td>
<td>(22.8)</td>
</tr>
<tr>
<td>Emission ( \lambda_{max} ), nm</td>
<td>535</td>
<td>510</td>
<td>538</td>
</tr>
<tr>
<td>( 10^6 \rho ) (air-saturated)</td>
<td>( a )</td>
<td>3.1</td>
<td>2.4</td>
</tr>
<tr>
<td>( 10^6 \rho ) (argon-saturated)</td>
<td>8.1</td>
<td>6.8</td>
<td>15.9</td>
</tr>
<tr>
<td>Stokes shift, cm(^{-1} )</td>
<td>17 000</td>
<td>15 900(^{\circ} )</td>
<td>18 000</td>
</tr>
<tr>
<td>Emission lifetime, ( \tau ) (nm)</td>
<td>( c )</td>
<td>( c )</td>
<td>17 \pm 1</td>
</tr>
</tbody>
</table>

\* Owing to rapid thermal oxidation, reliable quantum yields could not be determined. \# Based on the average of both absorption maxima of the \( A \) band. \$ Owing to photochemical instability, reliable lifetimes could not be determined. \^ Single-exponential decay.
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Figure 4. Qualitative MO scheme of MC13- (M = Ge, Sn, Pb) in D3h (trigonal-planar) and C3v (trigonal-pyramidal) symmetry (Walsh diagram). * orbitals of the ligands are omitted.

Figure 5. Qualitative potential energy diagram of SnCl3-

and tetrahedral structures. The rather large Stokes shift which we observed for MCl3- and MCl32- is certainly caused by the elimination of the ground-state distortion in the excited state.

Our suggestion that the distortion of s2 metal complexes is eliminated by sp excitation is not a completely new idea. A similar approach has been used before to explain the large Stokes shift of s2 ions doped into solid matrices. In the ground state, the s2 ions can occupy off-center positions in large interstices formed by the anions, but in the sp excited state, they move toward the center.

In this context, it is quite interesting to note that the Stokes shift observed for many transition metal complexes is caused by an opposite effect. While d* metal complexes are mostly rather symmetrical in their ground states, they frequently undergo a distortion in the excited state.

Finally, the origin of the luminescence quenching of MCl3- and MCl32- by oxygen should be briefly discussed. Sn2+ has been known for a long time to undergo a facile photooxidation to Sn4+ by oxygen. Because of its potential application for electroless metal plating, this photoreaction was studied in some detail.

However, the nature of the reactive excited state was apparently not of any interest. In addition to Sn2+, other s2 ions such as Ti3+ and Sb3+ are also photooxidized in the presence of oxygen. It has been shown only recently that the photooxidation of Sb3+ to Sb5+ is caused by an excited-state electron transfer from Sn4+ to O2. Although the investigation of the photochemistry of the ions MCl3- was not within the scope of the present work, we note that SnCl3-, GeCl3-, and, with much smaller efficiency, also PbCl3- underwent a photooxidation by oxygen. It is assumed that these reactions occur by an excited-state electron transfer in analogy to the Sb5+ reaction.

Conclusion
Chloro complexes of s2 ions such as GeCl3-, SnCl3-, PbCl3-, and PbCl32- are luminescent under ambient conditions. While these complex ions have less symmetrical structures in their ground states in accordance with the VSEPR model, it is suggested that these complexes rearrange toward highly symmetrical geometries in the emitting metal-centered sp excited states.

Acknowledgment. Support of this research by the Deutsche Forschungsgemeinschaft (Grant Vo 211/8-1) and BMFT (Grant 0329075A) is gratefully acknowledged. We thank P. Huber for emission lifetime measurements.

References
(33) Nikol, H. Unpublished results.