Electronic Spectra and Photochemistry of Tin(II), Lead(II), Antimony(III), and Bismuth(III) Bromide Complexes in Solution

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Dedicated to Prof. Dr. Dr. h. c. mult. E. O. Fischer on the occasion of his 75th birthday

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Electronic Spectra, Bromo Complexes, Main Group Metals, Photochemistry

The electronic spectra of bromo complexes of main group metal ions with an s^2 electronic configuration ($SnBr_3^-$, $PbBr_3^-$, $PbBr_4^{2-}$, $SbBr_4^-$, $SbBr_6^{3-}$, $BiBr_4^-$, $BiBr_6^{3-}$) in acetonitrile show long-wavelength absorption bands which are assigned to metal-centered sp transitions. Compared to the corresponding chloro complexes the sp bands of the bromo complexes appear at longer wavelength due to sp/LMCT mixing (LMCT = ligand-to-metal charge transfer). As a result of this mixing the luminescence which originates from low-energy sp excited states is much weaker than that of the chloro complexes. Moreover, some of the bromo complexes (*e.g.* $BiBr_4^-$) undergo a photochemical redox decomposition induced by LMCT excitation.

Introduction

Main group metal ions with an s^2 electronic configuration such as Sn^{2+}, Pb^{2+}, Sb^{3+} and Bi^{3+} form a variety of halide complexes [1, 2] which exist as well-defined anions in organic solvents of low coordinating ability such as acetronitrile [3]. During recent years we studied the absorption and emission spectra of the chloro complexes of these s^2 metal ions in solution [3–10]. The longest-wavelength absorption and emission were assigned to metal-centered sp transitions. The energy of these transitions is dependent on the metal and the molecular structure. The present study was undertaken in order to investigate the influence of the ligands on the electronic spectra. It might be assumed that the metal-localized sp transitions are hardly affected by the ligands. However, some previous observations indicated that the influence of the ligands is not negligible. If chloride ligands are replaced by bromide the longest-wavelength absorptions of s^2 complexes are apparently shifted to lower energies [11–16]. A systematic study of the absorption as well as the emission spectra of the bromo complexes of Sn^{2+}, Pb^{2+}, Sb^{3+} and Bi^{3+} was expected to clarify the role of the ligands. This investigation should be supplemented by an exploration of the photochemical properties of the bromo complexes.

Experimental Section

Materials

The compounds $[NEt_4]SnBr_3$ [17, 18], $[NEt_4]SbBr_4$ [19, 20], and $[NEt_4]BiBr_4$ [19, 20] were prepared according to published procedures. $[NEt_4]PbBr_3$ was synthesized in analogy to $[NEt_4]PbCl_3$ [8, 21]. Acetonitrile was spectrograde.

Spectroscopy

Absorption spectra were measured with a 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 intensities of the bromo complexes with that of $[Ru(bipy)_3](PF_6)_2$ in acetonitrile (λ_{max} = 605 nm; ϕ = 0.013) [22] under identical conditions such as exciting wavelength, optical density, and apparatus parameters.

Photolyses

The light source was a Hanovia Xe/Hg 977 B-1 (1000 W) lamp. Monochromatic light was obtained by means of a Schoeffel GM 250-1 high-intensity monochromator. The photolyses were carried out at room temperature in 1 cm cells. Progress of photolysis was monitored by UV-visible spectrophotometry. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than

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5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated and equipped with a RkP-345 detector.

Results

Electronic spectra

The absorption and emission spectra of $SnBr_3^-$ and $PbBr_3^-$ in acetonitrile are shown in Fig. 1 and 2. The excitation spectra matched the absorption spectra rather well. While the absorption spectrum of $SnBr_3^-$ did not change upon addition of bromide, $PbBr_3^-$ underwent spectral changes including clear isosbestic points at 279 and 321 nm. According to an analysis of the spectral changes and their dependency on the concentration of added bromide $PbBr_3^-$ was converted into $PbBr_4^{2-}$. The equilibrium constant ($PbBr_3^- + Br^- \rightleftarrows PbBr_4^{2-}$) was surprisingly large (K = 13100 $Lmol^{-1}$). The absorption and emission spectra of $PbBr_4^{2-}$ are shown in Fig. 3. Again, the excitation spectrum agreed with the absorption spectrum.

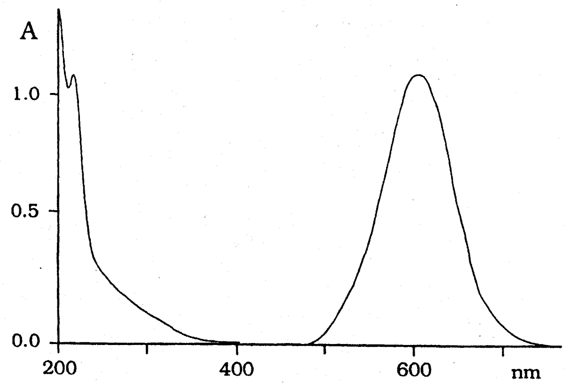

Fig. 1. Absorption (left side) and emission (right side) spectra of 1.4×10^{-4} M $[NEt_4]SnBr_3$ in CH_3CN at room temperature (1 cm cell; emission: $\lambda_{exc} = 310$ nm; intensity in arbitrary units).

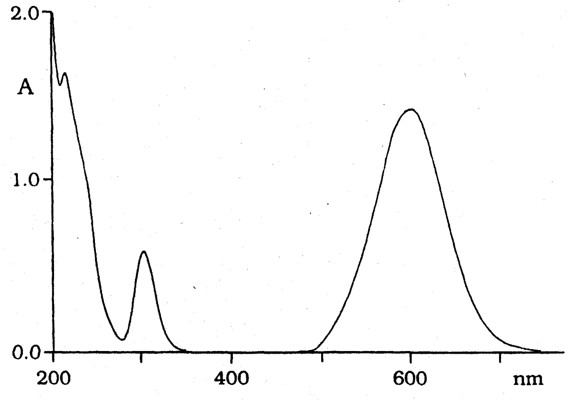

Fig. 2. Absorption (left side) and emission (right side) spectra of 1.3×10^{-4} M $[NEt_4]PbBr_3$ in CH_3CN at room temperature (1 cm cell; emission: $\lambda_{exc} = 310$ nm; intensity in arbitrary units).

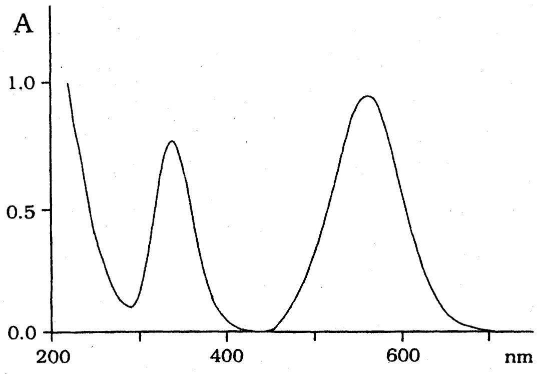

Fig. 3. Absorption (left side) and emission (right side) spectra of 1.6×10^{-4} M $[NEt_4]_2PbBr_4$ in CH_3CN at room temperature (1 cm cell; emission: $\lambda_{exc} = 370$ nm; intensity in arbitrary units).

The absorption spectra of $SbBr_4^-$ and $BiBr_4^-$ underwent also changes upon addition of bromide (Fig. 4 and 5). Both complexes were converted to $SbBr_6^{3-}$ (K = 310 L^2mol^{-2}) and $BiBr_6^{3-}$ (K = 5100 L^2mol^{-2}), respectively. The bromo complexes of Sb^{3+} and Bi^{3+} were not emissive in solution under ambient conditions.

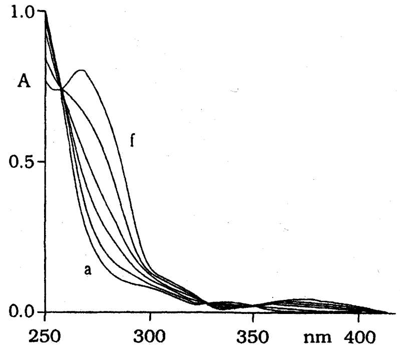

Fig. 4. Absorption spectrum of 0.7×10^{-4} M $[NEt_4]SbBr_4$ in CH_3CN in presence of (a) 0, 6.6×10^{-5}, 1.3×10^{-4}, 2.6×10^{-4}, 5.0×10^{-4} and (f) 9.6×10^{-4} M $[NEt_4]Br$.

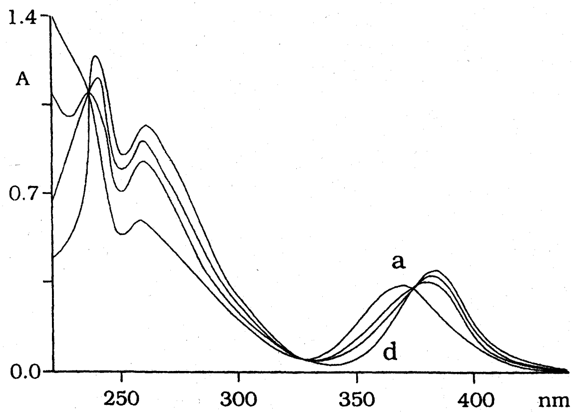

Fig. 5. Absorption spectrum of 3.5×10^{-4} M $[NEt_4]BiBr_4$ in CH_3CN in presence of (a) 0, 1.6×10^{-4}, 3.2×10^{-4} and (d) 1.3×10^{-3} M $[NEt_4]Br$.

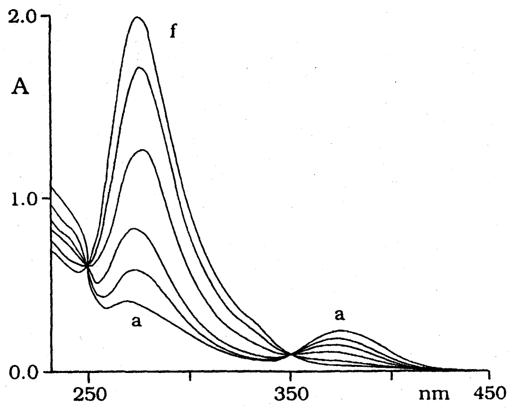

Fig. 6. Spectral changes during the photolysis of 1.2×10^{-4} M $[NEt_4]BiBr_4$ in CH_3CN at (a) 0, 5, 10, 20, 40 and (f) 100 s irradiation time ($\lambda_{irr} = 366$ nm; 1 cm cell).

The spectral data of all complexes are summarized in Table I.

Photochemistry

The photolysis of $BiBr_4^-$ in argon-saturated acetonitrile was accompanied by spectral changes (Fig. 6) which clearly indicate the formation of Br_3^- ($\lambda_{max} = 269$ nm; $\varepsilon = 5.5 \cdot 10^4$ Lmol^{-1} cm^{-1}) [23, 24]. The irradiation of $BiBr_4^-$ at higher concentrations (10^{-3} M) led to the appearance of a black precipitate of elemental bismuth. Since the photolysis of $BiBr_4^-$ yielded roughly equimolar amounts of tribromide it is assumed that $BiBr_4^-$ reacts according to the equation:

$$BiBr_4^- \rightarrow Bi(0) + Br_3^- + 1/2\,Br_2$$

Free bromine which must be also formed in the photolysis does not show up in the spectral changes since it does not absorb strongly in the UV/visible region [24]. $BiBr_4^-$ disappeared with quantum yields of ϕ = 0.45 at λ_{irr} = 306 nm,

Table I. Absorption and emission data for several bromo complexes of s^2 metal ions in solution at room temperature.

Complex		$SnBr_3^-$	$PbBr_3^-$	$PbBr_4^{2-}$	$SbBr_4^-$	$SbBr_6^{3-}$	$BiBr_4^-$	$BiBr_6^{3-}$
Absorption	A-Band [nm] (ε [Lmol^{-1} cm^{-1}])	320 (130) *sh*	306 (6800)	343 (1970)	334 (1180) *sh*	359 (920)	367 (4400)	384 (3800)
	B-Band [nm] (ε [Lmol^{-1} cm^{-1}])	275 (1790) *sh*	254 (12400)	–	300 (2370) *sh*	311 (2890) *sh*	–	274 (11230)
	C-Band [nm] (ε [Lmol^{-1} cm^{-1}])	217 (10500)	221 (22000)	–	245 (47600)	266 (21000)	259 (8100)	262 (13400)
	LMCT [nm] (ε [Lmol^{-1} cm^{-1}])	–	–	–	216 (36700)	–	232 (17550) *sh*	241 (17200)
Emission	λ_{max} [nm] ϕ (argon-sat.)	603 0.0046	604 0.086	560 0.018	– –	– –	– –	– –
Stokes shift [cm^{-1}]		16600	16500	17800	–	–	–	–

$\phi = 0.43$ at $\lambda_{irr} = 313$ nm, and $\phi = 0.30$ at $\lambda_{irr} = 366$ nm.

The photochemistry of the other bromo complexes was not studied in detail. However, it was observed that $PbBr_3^-$ in deaerated acetonitrile underwent also a photoredox decomposition with a concomitant deposition of the metal.

Discussion

Halide complexes of s^2 metal ions are characterized by metal-centered sp and ligand-to-metal charge transfer (LMCT) transitions at higher energies. This situation is exemplified by a qualitative MO scheme of an octahedral bromo complex of an s^2 metal ion (Fig. 7). Since an s^2 ion has an $^1S_0$ ground state and $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$ excited states the $a_{1g}^* \rightarrow t_{1u}^*$ sp transition splits in several components. Generally, three sp absorptions may be observed: A band ($^1S_0 \rightarrow {}^3P_1$ or $^1A_{1g} \rightarrow {}^3T_{1u}$ in O_h symmetry), B band ($^1S_0 \rightarrow {}^3P_2$ or $^1A_{1g} \rightarrow {}^3T_{1u}$) and C band ($^1S_0 \rightarrow {}^1P_1$ or $^1A_{1g} \rightarrow {}^1T_{1u}$) [25–27]. LMCT transitions involve the promotion of a ligand electron from the filled p_π orbitals (t_{2u}, t_{1g}, t_{2g}) and p_σ orbitals (e_g, t_{1u}, a_{1g}) to the empty antibonding p_σ orbitals (t_{1u}^*) of the metal (Fig. 7) [13]. The bromide s_σ orbitals (e_g, t_{1u}, a_{1g}) could be too stable to be involved in low-energy LMCT transitions.

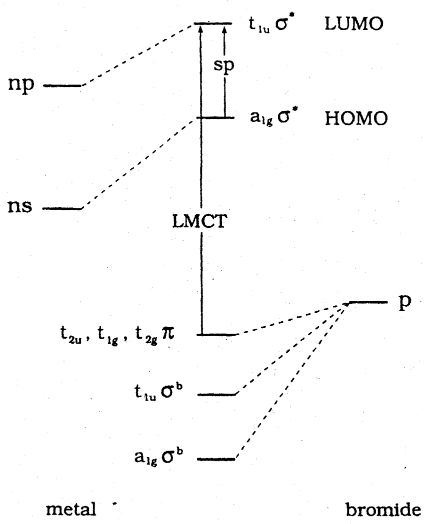

Fig. 7. Qualitative MO scheme and electronic transitions of an octahedral bromo complex of an s^2 metal ion.

In the case of the chloro complexes LMCT transitions may occur only at rather high energies. In fact, all long-wavelength transitions of the chloro complexes of Sn^{2+}, Pb^{2+}, Sb^{3+}, and Bi^{3+} were assigned to metal-centered sp transitions [3, 7, 8]. The interpretation of the spectra of the corresponding bromo complexes is less straight-forward since bromide is a stronger reductant and LMCT absorptions are expected to appear at longer wavelength. They may thus obscure the sp bands.

As a further complication sp and LMCT transitions can mix. The bromide valence orbitals occur at relatively high energies and are thus close to the metal s orbital. The large σ-overlap shifts then the a_{1g}^* orbital (Fig. 7) to higher energies and increases the ligand contribution to this MO. Since the metal p orbitals are much less stable than the s orbital the σ-overlap between metal p and ligand orbitals is apparently smaller. As an overall effect the sp transition $a_{1g}^* \rightarrow t_{1u}^*$ of bromo complexes is displaced to lower energies and contains an increased LMCT contribution compared to the corresponding chloro complexes.

A comparison of the absorption spectra shows clearly that the bromo complexes absorb at longer wavelength (Table I) than the corresponding chloro complexes of Sn^{2+}, Pb^{2+}, Sb^{3+}, and Bi^{3+} [3, 7, 8]. We suggest that this red shift is a strong indication for considerable sp/LMCT mixing in the case of the bromo complexes. In this context it is of interest that halide complexes of d^{10} ions such as Cu^+ [28] or Ag^+ [29] show similar effects. Metal-centered ds transitions mix apparently with appropriate LMCT transitions [28, 30].

The sp absorptions of the bromo complexes Sn^{2+}, Pb^{2+}, Sb^{3+}, and Bi^{3+} (Table I) were assigned in analogy to those of the corresponding chloro complexes [3, 7, 8] assuming comparable energy differences between A, B and C bands. Deviations of the spectral pattern between chloro and bromo complexes are then partially due to additional long-wavelength LMCT bands which appear in the spectra of the bromo complexes (Table I). More detailed and reliable assignments are hampered by the low symmetries of the MX_m^{n-} complexes with m = 3 (C_{3v}) and 4 (C_{2v}) [3].

The assumption of considerable sp/LMCT mixing in bromo complexes of s^2 metal ions is also supported by other observations. The luminescence of the bromo complexes (Table I) is much weaker than that of the corresponding chloro complexes. The anions $SbBr_4^-$, $SbBr_6^{3-}$, $BiBr_4^-$ and $BiBr_6^{3-}$ do not emit at all. Generally, the luminescence of main group metal complexes originates from sp excited states, while LMCT states are deactivated by other processes including photoreactions [3, 6, 9, 31]. The low emission quantum yields of the bromo complexes are thus a good indication of a notable sp/LMCT mixing in the lowest excited states.

The Stokes shifts of the luminescence of the bromo complexes (Table I) are comparable to those of the corresponding chloro complexes [3, 7, 8]. The structural changes which take place in the emitting excited states of the bromo complexes are apparently very similar to those which occur upon sp excitation of the chloro complexes [3, 7, 8].

The partial LMCT character of the lowest excited states of the bromo complexes is also evident from their photoactivity. While the chloro complexes of s^2 metal ions undergo a photooxidation by intermolecular excited state electron transfer to molecular oxygen [4, 6, 9] the irradiation of the bromo complexes may also lead to the reduction of the metal and oxidation of the bromide ligands. This process which is typical for LMCT excitation [4, 6, 9, 31] is most efficient at shorter wavelength where LMCT transitions are expected to occur. The reduction of the photochemical quantum yield with increasing wavelength of irradiation is an indication that the LMCT contribution to the lower excited states becomes smaller but cannot be neglected. A similar wavelength-dependent quantum yield was also observed for the photochemical reductive elimination of $TeBr_6^{2-}$ [31]. Contrary to the previous interpretation we now suggest that this dependency on the irradiation wavelength is also caused by sp/LMCT mixing which decreases with the excitation energy.

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