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The Structures of s^2 Metal Complexes in the Ground and sp Excited States

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Generally, the ground state structures of simple molecular complexes with s^2 metal ions such as Ge^{2+} , Sn^{2+} , Pb^{2+} , Sb^{3+} , and Bi^{3+} are in agreement with the VSEPR model. The geometries are determined by a stereochemically active lone pair although there are exceptions to this rule. In terms of qualitative MO considerations these VSEPR structures are the result of a second order Jahn–Teller effect. Highly symmetrical geometries are less stable since they are characterised by a strongly antibonding s^2 electron pair with a spherical distribution (inert pair). A stabilisation is achieved by a distortion which lowers the energy of this electron pair by sp orbital mixing. Simultaneously, this pair becomes stereochemically active (lone pair). Generally, the lowest electronically excited states of s^2 complexes are of the metal centered sp type. In the sp state the distortion is no longer favored. Accordingly, this distortion is eliminated. As a result the emission from sp states is associated with very large Stokes shifts.

Key Words: s^2 metal complexes, structures, distortions, absorption, luminescence, excited states

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INTRODUCTION

Coordination compounds of ions with an s^2 electron configuration such as Ge^{2+} , Sn^{2+} , Pb^{2+} , Sb^{3+} , Bi^{3+} , and Te^{4+} play an important role in the chemistry of main group metals. These complexes exist in a variety of coordination numbers and structures.^{1,2} In the solid state polymeric structures and three-dimensional networks are frequently observed. A simple correlation between electronic structure and geometry does not seem to exist. However, the structures of molecular s^2 complexes can be predicted by the VSEPR (valence shell electron pair repulsion) model developed by Gillespie and Nyholm,³ although there are exceptions to these rules. The VSEPR model is supported by qualitative MO arguments which have been nicely elaborated by Albright, Burdett and Whangbo.⁴ We anticipated that the electronic spectra of s^2 complexes might improve our understanding of their structures. Since s and p orbitals of the s^2 ions are involved in the bonding interactions with ligands, the metal-centered sp transitions should be well suited as a probe for the investigation of the electronic and geometrical structures in the ground as well as in the excited state.

When we started this work we found it quite surprising that the electronic spectra of molecular s^2 complexes had been largely ignored in the past.⁵ While some information on the absorption spectra has been available,⁶ very little has been known about the emission spectra despite the fact that the first observation on the luminescence of s^2 ions had been reported more than 50 years ago.⁷ In contrast to molecular complexes in solution the electronic absorption and emission spectra of s^2 ions doped into suitable matrices have been studied extensively.^{8,9} We expected that these results should facilitate the investigation of the electronic spectra of coordination compounds of s^2 ions under ambient conditions. We felt that our first observations and conclusions are of general interest and justify the presentation of this account.

THE VSEPR MODEL

According to the VSEPR model³ the number of σ -bonding electron pairs, which are provided by the ligands, and one electron pair,

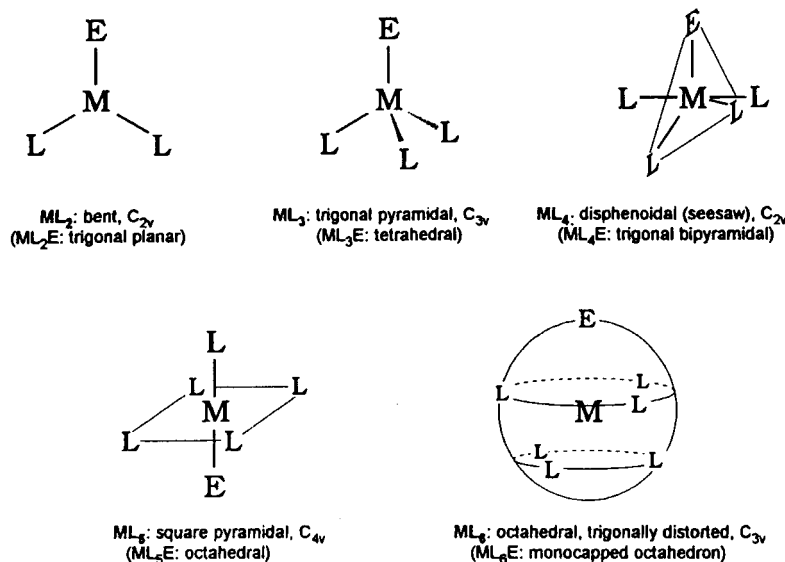


FIGURE 1 Simplified molecular structures of s^2 complexes $ML_2(ML_2E)$ to $ML_6(ML_6E)$ according to the VSEPR model (E = lone pair).

which originates from the s^2 ion, determine the structure of s^2 complexes. All electron pairs together occupy the positions of a highly symmetrical polyhedron. One of these positions is reserved to the stereochemically active lone pair (E). The complex itself then has a structure which is distorted when compared to the highest possible symmetry. The structures of the coordination numbers 2 (ML_2) to 6 (ML_6) are illustrated in Fig. 1.

$SnCl_2$ and $SnBr_2$ are suitable examples of ML_2E complexes. However, since they are characterised by an electron sextet at the metal they are electronically unsaturated and are not stable in the condensed phase under ambient conditions. Nevertheless, $SnCl_2$ and $SnBr_2$ exist as bent molecules in the gas phase¹⁰ in accord with the VSEPR model while polymeric structures are formed in the solid state.^{11,12}

The ions $GeCl_3^-$, $SnCl_3^-$, and $PbCl_3^-$ are trigonal pyramidal in solution^{13,14} and partially in the solid state.^{11,15-18} These complexes represent the ML_3E structure. Although they are not metal complexes, carbanions CR_3^- belong to the same structural type. How-

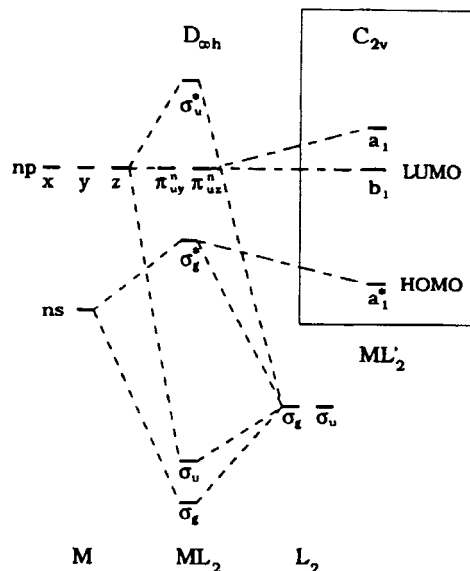


FIGURE 2 Qualitative MO-scheme of a linear complex ($D_{\infty h}$) and its distortion to a bent structure (C_{2v}); π -orbitals of the ligands are omitted.

ever, due to π -bonding deviations are possible.^{19,20} For example, $C(CN)_3^-$ is not trigonal pyramidal but trigonal planar²¹ (see below).

The anions $SbCl_4^-$ and $BiCl_4^-$ and probably $PbCl_4^{2-}$ have disphenoidal structures in solution^{22,23} and thus correspond to the ML_4E type.

Examples of ML_5E complexes are rare, but SbF_5^{2-} exists in the square pyramidal geometry.²⁴

ML_6E complexes are of special interest. While the non-metallic s^2 molecule XeF_6 ²⁵ indeed forms an octahedron which is trigonally distorted, other s^2 complexes such as $SbCl_6^{3-}$,²⁶⁻²⁸ $BiCl_6^{3-}$,^{27,29} and $TeCl_6^{2-}$ ^{30,31} are exceptions to the VSEPR rules. They are octahedral. The s^2 electron pair is then not stereochemically active but remains inert.

MO SCHEMES (WALSH DIAGRAMS) OF S^2 COMPLEXES

In terms of qualitative MO theory the electronic and geometrical structures of s^2 complexes are best understood when we look first

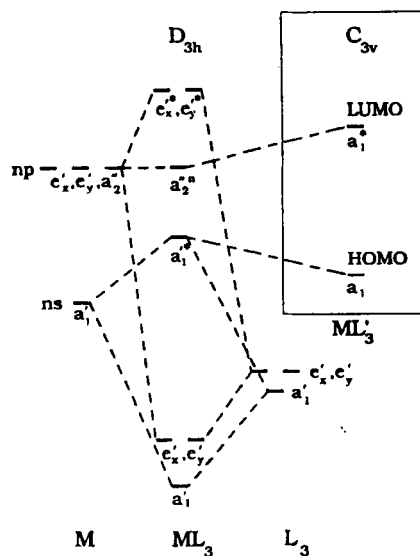


FIGURE 3 Qualitative MO-scheme of a trigonal planar complex (D_{3h}) and its distortion to a trigonal pyramidal structure (C_{3v}); π -orbitals of the ligands are omitted.

at hypothetical structures which are highly symmetrical.⁴ In each case the σ MO which is derived from the metal s orbital would be strongly antibonding. Since this HOMO is occupied by two electrons the highly symmetrical structures are not stable but distort toward geometries which lower the energy of the HOMO. A suitable distortion transforms this σ_s^* orbital and one of the empty p orbitals to MOs of the same symmetry. The σ_s^* and an appropriate p orbital will then mix. This mixing (or configuration interaction, hybridisation) stabilizes the HOMO. Simultaneously, the HOMO gains some p character and becomes stereochemically active. In contrast a p orbital based LUMO is destabilised by the admixture of s character. This second-order Jahn–Teller effect is illustrated on the basis of Walsh diagrams. We have adopted these diagrams from the book published by Albright, Burdett and Whangbo.⁴ The ligand π -orbitals are omitted for clarity. However, in some cases (see below) the structures are affected by π -bonding.^{19,20}

Let us now look at the MO schemes of highly symmetrical s^2

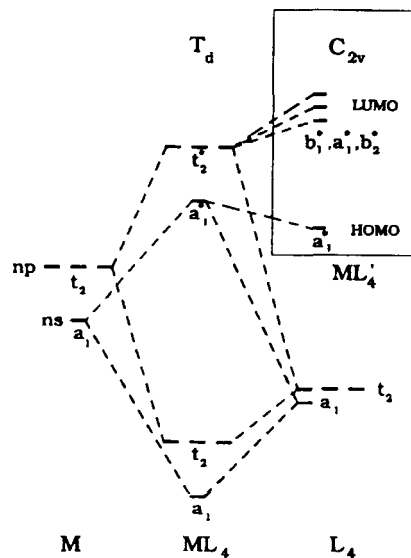


FIGURE 4 Qualitative MO-scheme of a tetrahedral complex (T_d) and its distortion to a disphenoidal structure (C_{2v}); π -orbitals of the ligands are omitted.

complexes and the influence of suitable distortions on the frontier orbitals which are derived from the metal s and p orbitals.

ML_2 complexes such as $SnCl_2$ (in the gas phase) are not linear ($D_{\infty h}$) but bent (C_{2v}). Bending of the molecule transforms the σ_s^* orbital and one of the nonbonding p orbitals to the same symmetry (a_1). The bent structure is thus stabilised by sp (a_1) mixing which lowers the energy of the σ_s^* orbital (Fig. 2).

Analogously, ML_3 complexes such as $GeCl_3^-$, $SnCl_3^-$, and $PbCl_3^-$ are not trigonal planar (D_{3h}) but distorted to a trigonal pyramidal structure (C_{3v}) which is again stabilised by an sp orbital mixing (Fig. 3). While this type of distortion also applies to most carbanions CR_3^- , π -bonding can lead to a trigonal planar structure for carbanions such as $C(CN)_3^-$.^{20,21} In this case the HOMO (p_z) is not stabilised by sp orbital mixing but by overlap with the π^* orbitals of the CN substituents which act as π -acceptor ligands in analogy to transition metal complexes.

Tetrahedral (T_d) ML_4 complexes are also not stable. A distortion

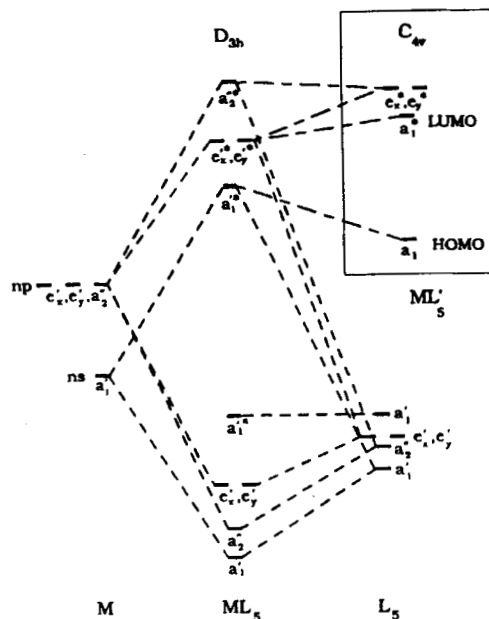


FIGURE 5 Qualitative MO-scheme of a trigonal bipyramidal complex (D_{3h}) and its distortion to a square pyramidal structure (C_{4v}); π -orbitals of the ligands are omitted.

to a disphenoidal (or seesaw, butterfly) structure C_{2v} allows for sp (a_1) orbital mixing and leads to a stabilisation of the HOMO (Fig. 4). The complexes $PbCl_4^{2-}$, $SbCl_4^-$, and $BiCl_4^-$ are examples of this geometry.

ML_5 complexes may be expected to be trigonal bipyramidal (D_{3h}). However, the antibonding HOMO (σ_s^*) can be stabilised by sp orbital mixing (Fig. 5) if the complex changes its structure to a square pyramid (C_{4v}) which has been found for SbF_5^{2-} .

ML_6 complexes should be not octahedral but undergo a trigonal distortion (C_{3v}) in order to lower the energy of the antibonding a_{1g} HOMO by sp configuration interaction (Fig. 6). Contrary to this expectation complexes such as $SbCl_6^{3-}$, $BiCl_6^{3-}$, and $TeCl_6^{2-}$ remain indeed octahedral. It is conceivable that at high coordination numbers a distortion would require too much space. As an alternative a reduction of the coordination number may take place.

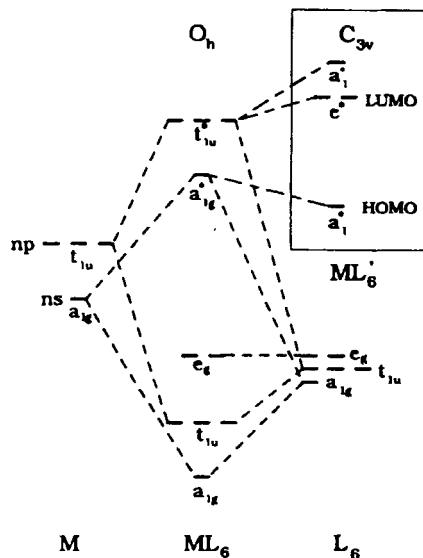


FIGURE 6 Qualitative MO-scheme of an octahedral complex (O_h) and its distortion to a trigonal bipyramidal structure (C_{3v}); π -orbitals of the ligands are omitted.

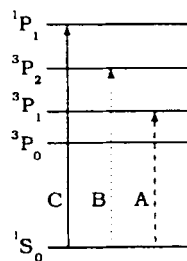


FIGURE 7 Energy level scheme of a free s^2 ion.

ABSORPTION SPECTRA

The absorption spectra of simple s^2 complexes can be analysed in terms of the sp transitions of the free s^2 ion⁸ (Fig. 7). The $^1S_0 \rightarrow ^3P_0$ transition is strongly forbidden and not observed. The spin-forbidden transitions to the 3P_1 and 3P_2 levels give rise to the so-called A and B bands which are of moderate intensity. The C band is more intense and belongs to the spin-allowed $^1S_0 \rightarrow ^1P_1$ transi-

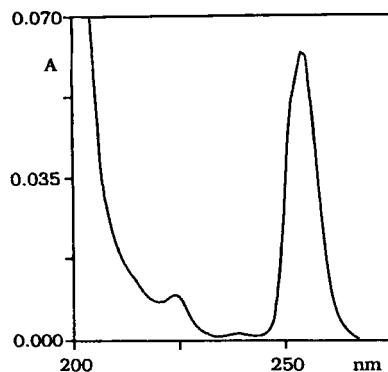


FIGURE 8 Absorption spectrum of a $\approx 10^{-7}$ M solution of elemental mercury in cyclohexane.

tion. The energies of these bands depend on the central metal, the ligands and the structure of the complexes. In addition to the metal-centered sp bands ligand-to-metal charge transfer (LMCT) absorptions may appear at shorter wavelength if the metal is oxidising (e.g., TeCl_6^{2-} ^{30,31}). The corresponding transitions terminate at the empty p orbitals of the metal.

For a free s^2 ion or atom the sp transitions should appear as absorption lines. In this context it is quite interesting that solutions of mercury “atoms” do not display sharp absorption lines. A broadening occurs due to the perturbation of the atoms by the solvent (Fig. 8). The A band corresponds to the well-known 254 nm line of atomic mercury in the gas phase.³²

In solution Tl^+ apparently does not form well-defined complexes with simple ligands such as halide or water.^{33,34} Owing to the low charge and large size (150 pm)¹ Tl^+ interacts only electrostatically with such ligands. The A band of the aquated Tl^+ ion appears at $\lambda_{\text{max}} = 213$ nm ($\epsilon = 4575$).³⁵ It is shifted to longer wavelength by the addition of halide.^{35,36}

Straightforward band assignments can be made for octahedral complexes such as SbCl_6^{3-} ,^{26,37,38} BiCl_6^{3-} ,³⁸ or TeCl_6^{2-} .^{30,31} In O_h symmetry the sp transitions $^1S_0 \rightarrow ^3P_1$, 3P_2 , and 1P_1 transform simply to $^1A_{1g} \rightarrow ^3T_{1u}(^3P_1)$, $^3T_{1u}(^3P_2)$ and $^1T_{1u}(^1P_1)$. All transitions are parity allowed. The two lowest-energy transitions are

TABLE I
Absorption and emission data for several s^2 complexes in solution at room temperature.

Group Number	13		14		15		16	
	Element	Tl(I)	Ge(II)	Sn(II)	Pb(II)	Sb(III)	Bi(III)	Tc(IV)
Complex	Tl ⁺	GeCl ₃ ⁻	SnCl ₃ ⁻	PbCl ₃ ⁻	PbCl ₂ ⁻	SbCl ₄ ⁻	BiCl ₄ ⁻	TcCl ₆ ²⁻
A-Band [nm]	213	280	292,272	273	294	283	319	410,385
(ϵ [l mol ⁻¹ cm ⁻¹])	(4575)	(30)	(300,700)	(8100)	(8200)	(1600)	(5100)	(700,1900)
B-Band [nm]	-	-	-	-	-	225	-	323
(ϵ [l mol ⁻¹ cm ⁻¹])	-	-	-	-	-	(3500)	-	(3000)
C-Band [nm]	-	218,225	216,226, 236	205	-	235	227	304,287, 277
($\epsilon \cdot 10^{-3}$ [l mol ⁻¹ cm ⁻¹])	-	(4,9,4,8)	(12,9,17,3, 14,0)	(22,8)	-	(5,0)	(12,3)	(8,0,9,0, 8,6)
Emission	370	535	510	538	518	740	720	475
λ_{max} [nm]	0.52	0.081	0.068	0.159	0.144	0.0061	0.01	0.004
ϕ (argon-sat.)	0.36 ± 0.08	^b	^b	17 ± 1	68 ± 2	1.2	<0.2	1.8
Lifetime [μs]								
Stokes Shift [cm ⁻¹]		17000	15900	18600	14700	21800	17500	9000

^aOnly an emission at 77 K was observed.

^bOwing to photochemical instability, reliable lifetimes could not be determined.

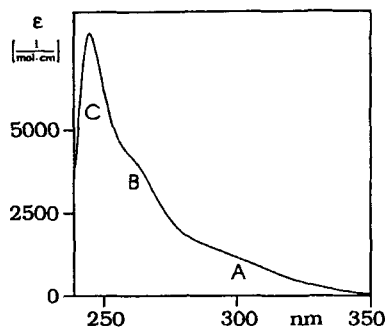


FIGURE 9 Absorption spectrum with band assignments of $[\text{SbCl}_6]^{3-}$ in CHCl_3 .

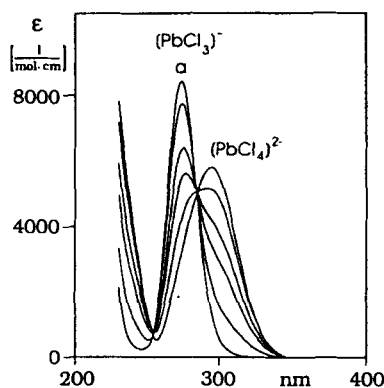


FIGURE 10 Absorption spectrum of $[\text{NEt}_4][\text{PbCl}_3]$ without $[\text{NEt}_4]\text{Cl}$ (a) and in the presence of increasing chloride concentration.

spin-forbidden and derived from two different excited states of the s^2 ions (3P_1 and 3P_2). Examples are given in Table I and Fig. 9.

Owing to the lower symmetries of the s^2 complexes with smaller coordination numbers detailed assignments are difficult to make. However, the basic pattern of the absorption spectra of simple s^2 complexes is always the same since the spectra are characterised by the appearance of the A, B, and C bands of the free s^2 ions (Table I). It is quite interesting and important that the absorption spectra do not depend very much on the coordination number and geometry of the complexes. This behavior is illustrated by the absorption spectra of PbCl_3^- and PbCl_4^{2-} ³⁹ (Fig. 10) or SbCl_4^- and SbCl_6^{3-} ³⁸ (Fig. 11).

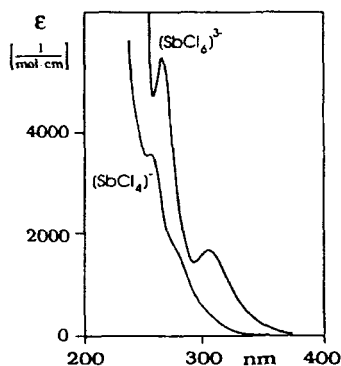


FIGURE 11 Absorption spectrum of $[\text{SbCl}_6]^{3-}$ and $[\text{SbCl}_4]^-$ in CH_3CN .

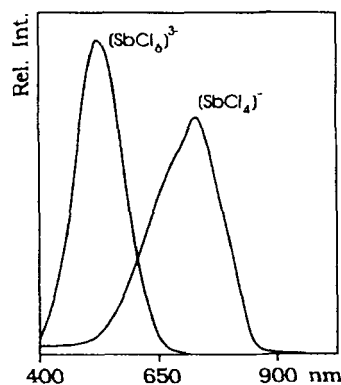


FIGURE 12 Emission spectra of $[\text{SbCl}_6]^{3-}$ and $[\text{SbCl}_4]^-$ in CH_3CN at room temperature.

EMISSION SPECTRA

Generally, s^2 complexes are photoemissive in solution under ambient conditions.⁵ While there is much evidence that the luminescence can be related to the sp excited 3P_1 state of the free s^2 ion the large Stokes shifts of the $^1S_0 \leftrightarrow ^3P_1$ transition of most s^2 complexes are only compatible with considerable changes of the molecular structure.

Relatively small Stokes shifts are observed for the octahedral complexes SbCl_6^{3-} and BiCl_6^{3-} ³⁸ (Fig. 12, Table I). Light absorp-

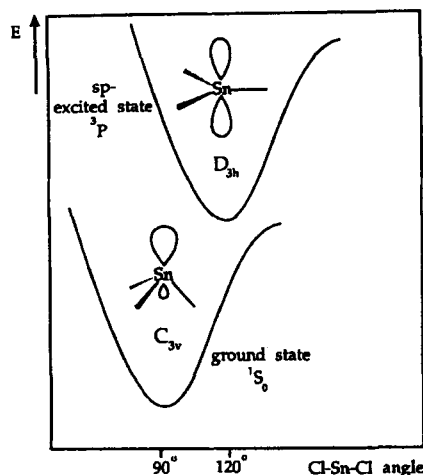


FIGURE 13 Qualitative potential energy diagram of SnCl_3^- .

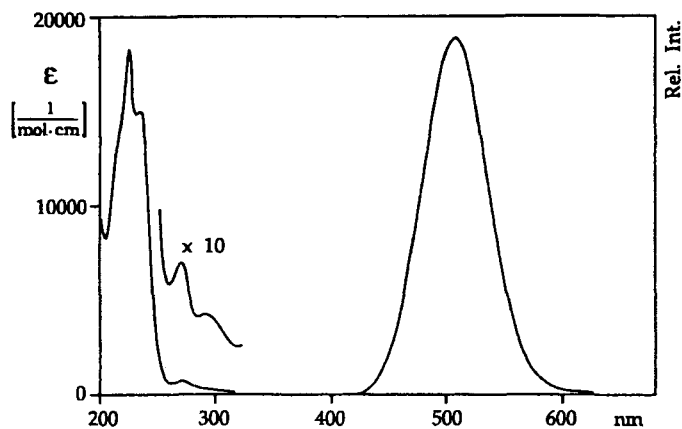


FIGURE 14 Absorption (left side) and emission spectrum (right side) of $[\text{NEt}_4][\text{SnCl}_3]$ in CH_3CN at room temperature.

tion by the A bands is associated with the $^1A_{1g}(^1S_0) \rightarrow ^3T_{1u}(^3P_1)$ sp transition which leads to the population of the triply degenerate t_{1u} p orbitals. The sp excited state is then expected to undergo a first-order Jahn-Teller distortion which should be responsible for the Stokes shifts.^{26,40}

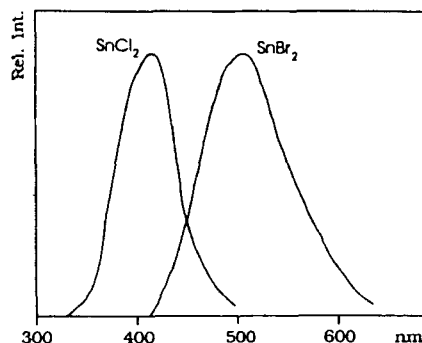


FIGURE 15 Chemiluminescence spectra (flame test) of SnCl_2 and SnBr_2 .

Much larger Stokes shifts are observed for SbCl_4^- or BiCl_4^- .³⁸ We suggest that these complexes which are distorted in their ground states (see above) eliminate this distortion in their sp excited state. This rearrangement accounts for the huge Stokes shifts (Table I, Figs. 11 and 12). This symmetrisation by sp excitation can be understood on the basis of the Walsh diagram (Fig. 4). The stabilisation of the disphenoidal ground state structure of MCl_4^- (including PbCl_4^{2-}) is lost in the sp excited state since the energy gain of HOMO a_1 is compensated by the energy loss of the electron promoted to the LUMO. It follows that the sp excited complexes then relax to the stereochemically less demanding highly symmetric tetrahedral structure (Fig. 4). This large structural change which is associated with the elimination of the ground state distortion is consistent with the immense Stokes shifts.

The same concept can now be applied to ML_3 complexes such as MCl_3^- with $\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$.³⁹ Again, the less symmetrical trigonal pyramidal ground state structures are no longer stabilised in the $a_1 a_1^*$ sp excited state (Fig. 3) but rearrange toward the highly symmetrical trigonal planar geometry (Fig. 13) in accordance with the large Stokes shifts (Table I, Fig. 14) of these complex anions.

In this context the emission behavior of ML_2 complexes such as SnCl_2 and SnBr_2 would be of considerable interest. Unfortunately, these molecules do not exist in the condensed phase under ambient conditions (see above). The significance of gas phase absorption spectra which were reported for SnCl_2 ⁴¹ is not quite clear. A gas phase photoluminescence of SnCl_2 and SnBr_2 has not been ob-

served. However, the popular flame test for tin⁴² may be based on a gas phase chemiluminescence of SnCl₂ and SnBr₂ which emit blue and green light, respectively. The emission spectra of the blue and green flames which are generated by a bunsen burner in a yet unknown reaction show maxima (Fig. 15) at $\lambda = 420$ nm (SnCl₂) and 505 nm (SnBr₂)⁴³ which are tentatively assigned to the $^3P_1 \rightarrow ^1S_0$ transition.

Although the absorption spectra of SnCl₂ and SnBr₂ are not reliably known they are not expected to be very different from those of SnCl₃⁻ and SnBr₃⁻ (A band: $\lambda_{\max} = 310$ nm). It follows that the Stokes shift of SnX₂ ($\Delta E \approx 12100$ cm⁻¹) is clearly smaller than that of SnX₃⁻ ($\Delta E \approx 15800$ cm⁻¹).⁴⁴ The structural changes between the ground and sp excited state of SnX₂ should then also be smaller than those of SnX₃⁻. This assumption is supported by the Walsh diagram of ML₂ complexes (Fig. 2). Since the HOMO–LUMO sp transition terminates at a nonbinding p orbital (b₁) the bent structure of SnX₂ may be partially preserved in the sp excited state.

CONCLUSION

In accordance with the VSEPR model the majority of molecular s² complexes do not exist in highly symmetrical structures due to a strongly antibonding HOMO which is derived from the metal s orbital. Distorted ground state structures are stabilised by sp orbital mixing while in the sp excited state these distortions are eliminated as indicated by large Stokes shifts of the emission. This behavior is quite contrary to that of many transition metal complexes which are symmetrical in the ground state but undergo distortions by electronic excitation.

Acknowledgments

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