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Complexes of Tin(IV) and Lead(IV)

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The discussion of the photochemistry of coordination compounds is almost exclusively restricted to complexes of transition metals. Although some scattered observations on the light sensitivity of coordination compounds of main-group metals have been reported, this important aspect of inorganic photochemistry has been largely ignored. A general concept which relates characteristic excited states to typical reactions does not yet exist for complexes of main-group metals. Systematic investigations in this field are also of interest with regard to technical applications. To some degree the lack of knowledge of this part of inorganic photochemistry seems to be related to the kinetic lability of complexes of main-group metals. In many cases well-defined compounds do not exist in solution, particularly in water. However, in organic solvents which are weakly coordinating many main-group metal complexes dissolve without decomposition and are thus susceptible to detailed photochemical studies. We report here our observations of an efficient photochemical reductive elimination of the complex ions [Sn(N₃)₆]²⁻ and [Pb(N₃)₆]²⁻ in acetonitrile. The photolysis leads to the formation of Sn(II) or Pb(II) and molecular nitrogen. The compounds [C₂H₅Sn]₃Sn[Sn(N₃)₆] and [C₄H₉Sn][Pb(N₃)₆]₄ are soluble and thermally stable in some organic solvents. The electronic absorption spectrum of [Sn(N₃)₆]²⁻ in acetonitrile displays long-wavelength bands (Figure 1) at λ_{max} = 264 nm (ε = 4700) and λ_{max} = 236 nm (ε = 14000). Corresponding absorption bands of [Pb(N₃)₆]²⁻ (Figure 1) occur at 390 nm (ε = 7420; shoulder) and 318 nm (ε = 19500).

Upon light absorption, [Pb(N₃)₆]²⁻ (Figure 2) and [Sn(N₃)₆]²⁻ dissolved in acetonitrile underwent an efficient decomposition.


Communications to the Editor

Photochemical Reductive Elimination of Hexaazido Complexes of Tin(IV) and Lead(IV)

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Figure 7. Dependence of the mean-square dipole moment (solid lines) and its temperature coefficient (dashed lines) of 2,2'oxydi-N-carbazoleoxycarbazole on the conformational energies E₀ and E₁. Calculations were performed at 30 °C with E₀ = 1.0 and E₁ = 2.1 kcal mol⁻¹; γ = 46° and χ = ±45°.

Values of (μ²) and its temperature coefficient are respectively represented as solid and dashed lines in Figures 6 and 7. Figure 6 shows the variation of these two magnitudes with the χ and γ angles, computed at 30 °C with E₀ = E₀ = 0, E₀ = 1.0, and E₁ = 2.1 kcal mol⁻¹. As this figure shows, exact agreement between theoretical and experimental values of (μ²) is obtained with γ = 50° if the preferred orientations χ = ±45° are used, while to achieve this agreement with χ = 0 would require γ ≈ 70° which is out of the range determined from the analysis of the NCEC molecule (see above). However, with γ = 50° and χ = ±45°, the theoretical value of the temperature coefficient of (μ²) is roughly 0, in contrast with the small negative result shown in the Experimental Section.

Figure 7 shows the variation of (μ²) and d ln (μ²)/dT with the conformational energies E₀ and E₁, calculated with T = 30 °C, γ = 46°, χ = ±45°, E₀ = 1.0, and E₁ = 2.1 kcal mol⁻¹. As this figure indicates, the calculated value of (μ²) agrees with the experimental results when E₀ = -0.1 ± 0.1 and E₁ = 0.1 ± 0.1 kcal mol⁻¹ in good concordance with the results of conformational energy calculations (see above). The agreement between theory and experiment is not so satisfactory in the case of d ln (μ²)/dT. Thus, a slightly positive value of this magnitude is suggested by Figure 7 whereas a negative value was found in the Experimental Section.

The calculated values of (μ²) are insensitive to the conformational energies E₀ and E₁. Thus, variations of 1 kcal mol⁻¹ in E₀ and E₁ produce respectively modifications of 0.6% and 0.1% in (μ²). Consequently, the effect of these two conformational energies on d ln (μ²)/dT is also negligible.

In view of the foregoing analysis, we conclude that it is possible to obtain excellent agreement between theoretical and experimental values of (μ²) for the ODNCAC molecule using a reasonable set of parameters. However, the agreement is much poorer in the case of d ln (μ²)/dT, although this discrepancy could be in part due to the experimental error involved in the determination of a temperature coefficient. It should be pointed out in this regard that the temperature coefficients are in general relatively small quantities corresponding to changes of only a few tenths of a percent per degree. Consequently, they are difficult to determine with accuracy.

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Registry No. PFCZ, 10491-11-9; NCEC, 24650-61-1; ODNCAC, 10491-57-1; 2,2'-oxydiethyl chloroformate, 106-75-2; carbazole, 86-74-8.

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Figure 1. Electronic absorption spectra of 1.17 × 10⁻⁴ M [(C₆H₅)₆N]₂[Sn(N₃)₆] (a) and 8.51 × 10⁻⁵ M [(C₆H₅)₆As₂][Pb(N₃)₄] in acetonitrile; 298 K, 1-cm cell.

![Figure 1](image1.png)

Figure 2. Spectral changes during the photolysis of 7.62 × 10⁻⁴ M [(C₆H₅)₆As₂][Pb(N₃)₄] in acetonitrile at (a) 0 and (e) 10 min irradiation time, with λₐ = 333 nm and a 1-cm cell.

With a residual absorption of the photolysis product at 350 nm neglected, the quantum yield of disappearance of [Pb(N₃)₄]²⁻ was calculated from the decrease of extinction at this wavelength. At an exciting wavelength of λ = 333 nm [Pb(N₃)₄]²⁻ decomposed with Φ = 0.23. At a monitoring wavelength of λ = 236 nm the disappearance of [Sn(N₃)₄]²⁻ was determined. The complex underwent a photodecomposition with Φ = 0.21 at an exciting wavelength of 254 nm.

The photolysis was accompanied by the formation of molecular nitrogen. By volumetric gas analysis a stoichiometric ratio of N₂/[M(N₃)₄]²⁻ = 3 was established for both complexes. Accordingly, the photolyses can be described as reductive eliminations:

\[\text{[Mn}^\text{IV}(\text{N}_3)^3\text{]}^2- \xrightarrow{\lambda} \text{[M}^\text{II}(\text{N}_3)^2\text{]}^2 + 3\text{N}_2\]

The photolysis of [Sn(N₃)₄]²⁻ and [Pb(N₃)₄]²⁻ may take place either by a simultaneous two-electron reduction of the metals or by two subsequent one-electron steps generating Sn(III) or Pb(III) as short-lived intermediates. At 77 K the photolysis of [M(N₃)₄]²⁻ in a matrix of ethanol/CH₂Cl₂ (1:1) did not yield any evidence for the formation of M(III). Characteristic ESR signals of paramagnetic Sn(III)⁶ or Pb(III)⁶ could not be detected. However, during the photolysis the azide ligands were apparently oxidized to azide radicals which are well-known to decompose to nitrogen atoms and molecular nitrogen (N₂ + N₂) at low temperatures. Clear ESR signals of N atoms appeared in the photolysed samples of [Sn(N₃)₄]²⁻ and [Pb(N₃)₄]²⁻.

In their highest oxidation state the metals Sn(IV) and Pb(IV) have an empty valence shell (ns⁰np⁰). Metal-centered electronic transitions can obviously not occur in the normal energy region. Both metals are oxidizing with Pb(IV) more than Sn(IV). The optical electronegativities are 1.9 for Pb(IV) and 1.5 for Sn(IV). It follows that electronic absorption bands of simple M(IV) complexes are most likely of the ligand-to-metal charge-transfer (LMCT) type. In analogy to [PbCl₄]²⁻ both absorption bands of [Sn(N₃)₄]²⁻ or [Pb(N₃)₄]²⁻ may be assigned to CT transitions from ligand σ* and π* orbitals to empty σ* orbitals derived from the metal’s orbitals. In octahedral symmetry there are two allowed LMCT transitions, τ₂(σ*) → τ₁(σ*) and τ₂(π*) → τ₁(π*) with the former occurring at lower energies. The position of the longest wavelength band of [Sn(N₃)₄]²⁻ and [Pb(N₃)₄]²⁻ agrees well with the optical electronegativities of both metals and the azide ligand (≈ 2.8). However, in azido complexes the metal–ligand bonding is generally not linear but bent at the coordinating nitrogen atom. This bending lifts the degeneracy of the π* orbitals of the azide ligand which split energetically. Consequently, both absorption bands of each complex may be also assigned to transitions from the split π* ligand orbitals to the σ* metal orbital.

These two alternative assignments are both only of the LMCT type and thus are rather similar with regard to the electron distribution between metal and ligand in the excited state. As a third possibility one of the two absorption bands of [M(N₃)₄]²⁻ may be a σ* intraligand (IL) transition which is forbidden in the free ligand but can become allowed due to the bonding of the azide ligand. However, this IL transition of the complex should occur at about 220 nm as in the free ligand. The ions [Pb(N₃)₄]²⁻ and [Sn(N₃)₄]²⁻ do not exhibit such a band. In addition, the fact that both bands shift similarly to higher energies when lead is replaced by tin argues against the IL and supports the LMCT assignment.

The occurrence of a photochemical reduction of Pb(IV) or Sn(IV) and oxidation of the azide ligand is obviously related to the electron distribution of the LMCT state. However, the formation of stable redox products must take place by a decrease of the metal oxidation state by two units since one-electron reduction would generate Pb(III) and Sn(III), which do not form stable complexes. This behavior is quite analogous to that of [Pb(N₃)₄]²⁻, while many other transition-metal complexes such as Co(III) ammines undergo one-electron reductions of the metal upon LMCT excitation.

It should be emphasized again that a general picture that described the excited-state reactivity of main-group coordination compounds does not yet exist. As an outlook we anticipate more investigations of this largely neglected but rather interesting part of inorganic photochemistry.
Organolithium Addition to Aldehyde Dimethylhydrazones: A Highly Diastereocontrolled Synthesis of Threo 2-Amino Alcohols and (1R,2R)-(-)-Norpseudoephedrine

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Our investigations of adrenergic agents required a methodology for the enantioselective synthesis of various threo 2-amino alcohols. Recently, stereoselective strategies for construction of 2-amino alcohols have been described.2-8 One approach,9-11 organometallic additions to α-alkoxy imines and sulfimines, appeared attractive, although problematic. Hydrazones derivatives would eliminate the problems associated with imine derivatives; however, only limited10 or preliminary11 reports of their electrophilic reactions with organometallic reagents have appeared. The three diastereoselectivity would presume a chelation controlled (Cram cyclic model) intermediate12,13 which would provide a suitable route to three 2-amino alcohols obtained by hydrazonocly cleavage of the hydrazines.5,19 Various organometallic reagents (Grignard reagents were sluggish or unreactive, additives, and solvents were investigated in the reaction shown in Scheme I. Organolithium reagents in diethyl ether were successful and most suitable for our needs.16

Table I contains examples17 which demonstrate the high threo diastereoselectivity, organolithium reagent generality, and efficiency obtained under the reaction conditions.18 The trityl ether in entry 10 eliminates the chelating effect of the oxygen atom such that the erythro diastereomer is produced with good specificity consistent with a Cram open-chain model.19 Reactions of hydrazones 1-4 were unaffected by organocopper reagents.

This methodology provides optically active intermediates limited only by the availability of the starting hydrazones. The hydrazines obtained from entry 11 were converted to α-adrenergic antagonists enantioselectively.24

Sharpless' methodology25 for kinetic resolution provides access to hydrazines of known configuration. This has been exploited


(16) The presence of other solvents, required for the preparation of the organolithium reagents, had no deleterious effects.

(17) 1-4 were prepared in 80-90% yield from protected (R)-3-hydroxy-octenone by (1) O3/-10 OC/CH2Cl2; (2) (CH3)$/-78 OC to -30 OC; and (3) (CH3)$/-30 OC/Na2SO4/-30 /AC. (c) Sato, F.; Kobayashi, Y.; Takahashi, 0.; Chiba, T.; Takeda, Y.; Kusakabe, M. J. Chem. Soc. Chem. Commun. 1985, 1636-1638.

(18) (a) Cameron, D. A.; Phillips, B. T., unpublished results. See supplementary material for reaction scheme.