Absorption and Emission Spectrum of [Zn₄O(Acetate)₆]

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The electronic spectrum of [Zn₄O(acetate)₆] in solution is characterized by an absorption ($\lambda_{max.}$ = 216 nm) and emission ($\lambda_{max.}$ = 372 nm) band; it is assigned to a ligand-to-metal charge-transfer (LMCT) transition, which corresponds to the band-gap transition of the semiconductor ZnO.

In recent years very small semiconductor particles have been studied extensively. The decrease of particle size is associated with a change of the optical properties (quantum size effect) that are different from those of the bulk semiconductor.[1] A further reduction of the particle size would ultimately yield molecular dimensions. The optical properties of such molecular clusters which could be considered as being the smallest constituents of a semiconductor should be of considerable interest. We explored this possibility and selected the compound [Zn₄O(acetate)₆] as a molecular model for ZnO. While the optical properties of ZnO have been studied in detail,[2] the electronic spectra of [Zn₄O(acetate)₆] are as yet unknown. This complex seems to be well suited as a model for ZnO since the important structural features of both compounds are very similar.[3,4] A tetrahedron of four Zn²⁺ ions contains an oxide ion. Zn²⁺ is also co-ordinated tetrahedrally by oxygen. In the case of the complex the tetrahedral co-ordination of Zn²⁺ by oxygen is achieved by the central oxide and three bridging acetate groups. Even the Zn–O (ca. 1.97) and Zn–Zn (3.20 Å) bond distances for both compounds are almost identical.

The complex [Zn₄O(acetate)₆] is soluble in a variety of solvents such as benzene, CH₂Cl₂, and ethanol. The solvents have to be completely dry in order to avoid hydrolysis with the formation of ZnO. A complete spectrum of [Zn₄O(acetate)₆] (Figure 1) was recorded in ethanol which is transparent above 200 nm. The complex displays an absorption maximum at λ = 216 nm (ε = 62 200 mol⁻¹ dm³ cm⁻¹). Absorption spectra of Zn(acetate)₂ in ethanol and Zn(OH)₄²⁻ in water were also measured. These compounds did not show any absorption maximum above 200 nm.

Solutions of [Zn₄O(acetate)₆] emitted an intense photoluminescence at room temperature. In CH₂Cl₂ the luminescence appeared at $\lambda_{max.}$ = 372 nm (Figure 1). At λ_{exc} = 300 nm the quantum yield of emission was ϕ = 0.15.

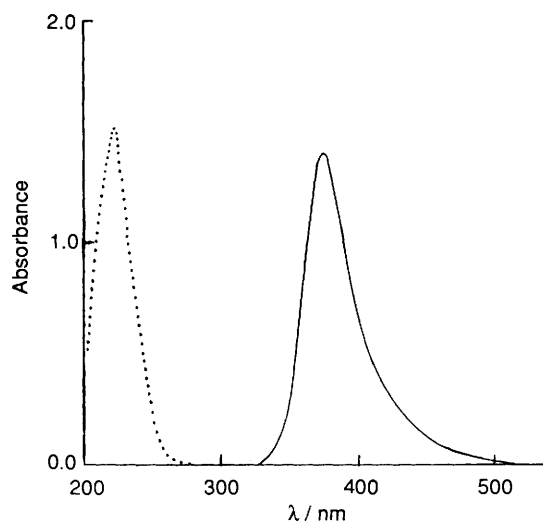**Figure 1.** Electronic absorption ($\cdots$) and emission (——) spectra of [$Zn_4O(acetate)_6$] at room temperature; 1 cm cell. Absorption: 2.43 × 10⁻⁵ M in EtOH. Emission: 1.15 × 10⁻⁴ M in CH_2Cl_2; $\lambda_{exc} = 300$ nm; intensity in arbitrary units.

The emission decayed with a life time of approximately $\tau = 10$ ns. The excitation spectrum of [$Zn_4O(acetate)_6$] in ethanol was in good accord with the absorption spectrum. Solutions of $Zn(acetate)_2$ or $Zn(OH)_4^{2-}$ did not show any photoluminescence.

Simple Zn^{2+} complexes such as ZnX_4^{2-} with X = halide[5] or OH^- do not show ligand-to-metal charge-transfer (LMCT) absorptions above 200 nm. The energy of the Zn^{2+} 4s orbital which is the acceptor orbital of a LMCT transition is apparently too high. On the contrary, the semiconductor ZnO absorbs at $\lambda_{os} \leqslant 365$ nm (os = onset of absorption).[1,2] In a molecular picture[2] this band-gap transition can be also considered as being an LMCT transition since the valence band of ZnO is composed of the filled oxide valence orbitals while the conduction band is formed by the empty Zn^{2+} 4s orbitals. The energy of the LMCT transition is expected to decrease as the number of the interacting valence orbitals at oxide and Zn^{2+} increases. Accordingly, a red shift of the band-gap transition is observed if the particle size increases from the smallest quantum size particles (λ_{os} ca. 310 nm) to bulk ZnO.[1,2] The electronic structure and the absorption spectrum of the molecular cluster can now be explained by using the same model.

The interaction of the four Zn^{2+} 4s orbitals of [Zn_4O(acet-

ate)₆] generates a bonding a_1 and three degenerate antibonding t_2 MOs (in T_d symmetry).[6] A similar interaction of the valence orbitals of the co-ordinating oxygen atoms should take place but is complicated by the fact that these oxygen atoms originate from the central oxide and the peripheral acetate ligands. In agreement with our qualitative model the oxide to a_1 (Zn^{2+}) LMCT transition ($\lambda_{max.} = 216$ nm) occurs at lower energies than that of mononuclear oxygen co-ordinated Zn^{2+} complexes [e.g. $Zn(acetate)_2$ or $Zn(OH)_4^{2-}$] but at higher energies than the band-gap absorption of ZnO particles which contain a much larger number of Zn^{2+} and oxide ions.

The luminescence properties are also quite interesting and informative. While mononuclear Zn^{2+} complexes have not been observed to show any emission (with the exception of a ligand-localized luminescence of Zn^{2+} complexes with ligands such as porphyrins[7] or 2,2'-bipyridyl[8]) the LMCT state of [$Zn_4O(acetate)_6$] luminesces strongly at $\lambda_{max.} = 372$ nm. The corresponding band-gap emission of ZnO occurs between $\lambda_{max.} = 320$ nm for small quantum size particles and $\lambda_{max.} = 380$ nm for the bulk.[2] The Stokes shift of the band-gap emission is very small since the electronic excitation of a semiconductor particle does not involve structural rearrangements. On the contrary, the Stokes shift ($\Delta\bar{v} = 19415$ cm⁻¹) of the luminescence of [$Zn_4O(acetate)_6$] is rather large. A considerable excited-state distortion of the molecular cluster may occur because the LMCT transition leads to the population of the bonding a_1 orbital. Similar interpretations were used to explain the emission behaviour of tetranuclear complexes of the d¹⁰ metals Cu¹,[9] Ag¹,[6] Au¹,[10] and Hg¹¹.[11]

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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