PHOTOLUMINESCENCE OF TETRAMERIC SILVER(I) COMPLEXES

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Received 1 February 1989

The tetrametric complexes $[AgP(OCH_3)_3Cl]_4$ and $[AgP(C_6H_5)_3Cl]_4$ show an emission which is assigned to a metal-centered 4d–5s transition. This emission occurs at rather low energies ($\approx 20800\ cm^{-1}$) due to modification of the ds transition by metal–metal interaction within the tetrahedral Ag_4 moiety of these clusters.

1. Introduction

In recent years we have observed photoluminescence of tetrameric Cu(I) [1] and Au(I) [2] clusters in solution or low-temperature glasses. This luminescence was assigned to a metal-centered s→d transition which is strongly modified by metal–metal interaction in the tetrameric d^{10} metal clusters. It is of interest whether Ag(I) as the third member of the first transition metal group will also be emissive. To our knowledge luminescence of a molecular coordination compound of Ag(I) has not yet been observed. This may be due, at least partially, to the well-known light sensitivity of silver compounds. However, in a matrix of alkali halides, Ag(I) has been shown to be luminescent [3–5]. Accordingly, in suitable cases emission from molecular Ag(I) complexes may be detected. In analogy to the luminescent $Cu(I)_4$ [1] and $Au(I)_4$ [2] clusters we selected tetrameric Ag(I) complexes as promising candidates for photoemission.

2. Experimental

The compounds $[AgP(OCH_3)_3Cl]_4$ [6], $[AgPPh_3Cl]_4$ [7,8], $\{Ag[P(OCH_3)_3]_4\}ClO_4$ [6,9], and $[Ag(PPh_3)_3Cl]$ [7,10] with $PPh_3=P(C_6H_5)_3$ were prepared according to published procedures. All substances were light sensitive and turned black following exposure to light due to the formation of metallic silver. Absorption spectra were measured in solution at room temperature on a Uvikon 860 absorption spectrometer. Emission spectra of the complexes in the solid state or in glasses of toluene ($[AgP(OCH_3)_3Cl]_4$) and toluene/pyridine ($[Ag(PPh_3)Cl]_4$) were obtained on a Hitachi 850 spectrofluorimeter equipped with a Hamamatsu 928 photomultiplier. The luminescence spectra were corrected for monochromator and photomultiplier efficiency.

3. Results

The absorption spectrum of $[AgP(OCH_3)_3Cl]_4$ is rather featureless and shows an increasing extinction towards shorter wavelength (fig.1) while the spectrum of $[AgPPh_3Cl]_4$ displays a pronounced absorption at $\lambda_{max}=249$ nm ($\epsilon=20000$). Both complexes are photoluminescent. Room temperature emission was only observed for solid $[AgP(OCH_3)_3Cl]_4$. At low temperatures (77 K) both complexes were emissive in the solid state as well as in glasses of organic solvents such as toluene. The emission of both complexes appeared at very similar wavelength with $\lambda_{max}=483$ nm for $[AgP(OCH_3)_3Cl]_4$ (fig. 1) and $\lambda_{max}=480$ nm for $[AgPPh_3Cl]_4$. This luminescence was independent of the excitation energy if light absorption by the solvents was excluded ($\lambda_{exc}>280$ nm).

For comparison we also searched for emission of

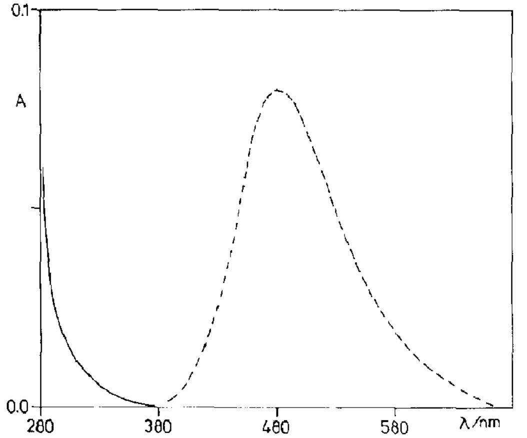

Fig. 1. Electronic absorption (——) and emission (---) spectra of $[AgP(OCH_3)_3Cl]_4$. Absorption: 7.63×10^{-4} M in toluene at room temperature, 1 cm cell. Emission: in toluene at 77 K; $\lambda_{exc}=320$ nm, intensity in arbitrary units.

the mononuclear complexes $\{Ag[P(OCH_3)_3]_4\}ClO_4$ and $[Ag(PPh_3)_3Cl]$. While the former complex did not luminesce under any conditions the latter showed an emission at $\lambda_{max}=434$ nm. Since this emission is identical to that of the free ligand PPh_3 it is attributed to PPh_3 impurities.

4. Discussion

The tetrameric clusters $[AgP(OCH_3)_3Cl]_4$ [11] and $[AgPPh_3Cl]_4$ [8] consist of a $[AgCl]_4$ cubane core and PR_3 as endstanding ligands. This structure was verified for the PPh_3 complex [8] and certainly applies also to the $P(OCH_3)_3$ complex. This assumption is supported by the similarity of the emission spectra of both compounds (see below). Within the cubane core the four silver ions form a tetrahedron. The metal–metal interaction of the Ag_4 moiety can be explained by a qualitative MO scheme [8,12] which includes the 4d and 5s orbitals of silver. The 5p orbitals are omitted since they occur at very high energies [13]. In T_d symmetry the 4d orbitals yield six bonding (a_1, e, t_2), eight nonbonding (e, t_1, t_2), and six antibonding (t_1, t_2) molecular orbitals (fig. 2). The 5s orbitals yield one bonding (a_1) and three antibonding (t_2) orbitals.

In the ground state the d orbitals are completely filled. The formal metal–metal bond order in the Ag_4 cluster is then zero. However, configuration interaction between 4d and 5s orbitals of the same symmetry (a_1 and t_2) leads to some stabilization of the appropriate d orbitals. This stabilization seems to be the origin of the metal–metal bonding in the clusters.

The absorption spectra of the clusters $[AgPR_3Cl]_4$ are not very instructive. Due to their limited solubility the compounds can be dissolved only in a few organic solvents such as toluene which are not transparent in the short-wavelength UV region. The $P(OCH_3)_3$ complex shows only an increasing extinction towards higher energies (fig. 1) while the PPh_3 compound is characterized by an intra-ligand band from coordinated PPh_3 at $\lambda_{max}=249$ nm. This band is common to all complex containing the $AgPPh_3$ moiety [14]. We assign the longest-wavelength band of $[AgP(OCH_3)_3Cl]_4$ to the lowest-energy ds transition from the HOMO (t_1 or t_2) to the LUMO (a_1). Since a band maximum was not identified down to 280 nm (fig. 1) the lowest-energy transition may be the symmetry-forbidden $t_1\rightarrow a_1$ instead of the allowed $t_2\rightarrow a_1$ transition. The low-intensity $t_1\rightarrow a_1$ ds band could thus be hidden under or obscured by shorter-wavelength bands of higher intensity such as the $t_2\rightarrow a_1$ band.

According to the MO scheme (fig. 2) the lowest-energy ds transition of the clusters $[AgPR_3Cl]_4$ must be red-shifted when compared with mononuclear Ag(I) complexes. The absorption spectra of simple Ag^+ species do indeed display their ds bands at rather high energies. In the free silver ion the $4d^95s^1$ excited state is located 39164 cm^{-1} above the $4d^{10}$ ground state [13,15]. In an aqueous solution of Ag^+ the corresponding absorption band was observed at $\bar{\nu}_{max}=44700$ cm^{-1} [15]. In matrices of alkali hal-

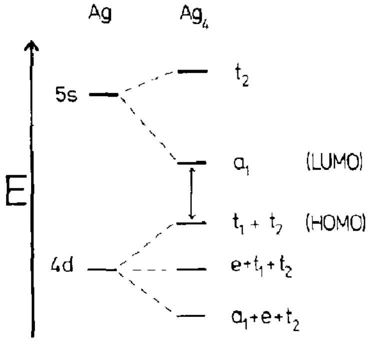

Fig. 2. Qualitative MO diagram of the tetrahedral $Ag(I)_4$ moiety.

ides the ds bands of Ag^+ occur in the same energy range but show vibrational structure [16].

The photoluminescence of $[AgP(OCH_3)_3Cl]_4$ and $[AgPPh_3Cl]_4$ is rather similar and appears near 20800 cm^{-1}. This emission is then logically assigned to the lowest-energy sd transition $a_1 \rightarrow t_1$ or t_2 (fig. 2). Since the lowest excited state is a triplet the emission may be a spin-forbidden transition from this triplet to the singlet ground state. Simple mononuclear Ag(I) complexes have not yet been reported as showing emission. We could also not detect any luminescence from $Ag[P(OCH_3)_3]_4^+$ and $[Ag(PPh_3)_3Cl]$ (see section 3). However, Ag^+ ions incorporated in alkali halide show an emission [3–5] ($\bar{\nu}_{max} = 40000$ cm^{-1} in NaCl) which was assigned to a spin-forbidden sd transition ($^3E_g \rightarrow {}^1A_{1g}$) [4,5]. In the tetrameric complexes this emission undergoes a large red-shift. This is certainly due, at least partially, to the decrease of the ds energy gap by metal–metal interaction in the clusters (fig. 2).

The emission of $[AgPR_3Cl]_4$ appears at much lower energies when compared to the absorption. It is assumed that this shift is associated with a considerable excited state distortion. We suggest that in analogy to tetrameric Cu(I) [1] and Au(I) [2] complexes, ds excitation leads to a strong contraction of the cluster since the formal bond order within the Ag_4 tetrahedron has increased from zero in the ground state to one in the ds excited state. The similarity of the emission of $[AgP(OCH_3)_3Cl]_4$ and $[AgPPh_3Cl]_4$ supports the assumption that the luminescence originates from the same ds excited state in both cases although the lowest-energy absorption of the PPh_3 complex is of the intra-ligand type. However, due to excited state distortion the energy of the equilibrated ds state is so low that it may easily drop below that of the intra-ligand state. In contrast the $P(OCH_3)_3$ complex does not provide low-energy intra-ligand states. The lowest-energy transition in absorption and emission is now certainly of the ds type.

Acknowledgement

Support of this research by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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