ABSORPTION AND EMISSION SPECTRA OF TETRAMERIC GOLD(I) COMPLEXES

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The lowest-energy absorption and emisson bands of the complexes [Au(dithioacetate)]$_4$ and [Au(piperidine)Cl]$_4$ are assigned to a metal-centered 5d–6s ($A_{2g} \leftrightarrow A_{1g}$) transition which is modified by the metal–metal interaction in the square-planar Au(1)$_4$ moiety.

1. Introduction

Coordination compounds with a d^{10}-electron configuration at the metal, such as Cu(I), Ag(I), and Au(I), have a remarkable tendency to form clusters [1]. At first sight this seems rather surprising since with a filled d shell, d-orbital interaction should not yield any metal–metal bonding. However, some bonding can result from the stabilization of d-orbital-based MOs by configuration interaction (CI) with appropriate empty MOs derived from the higher-energy s and p metal orbitals [1]. This type of CI is also important for the metal–metal interaction of certain square-planar d^8 complexes as indicated by absorption and emission spectroscopy [2,3]. Recently, we applied this general idea of d/s CI to the interpretation of the electronic spectra of the tetrameric clusters [Cu(I)LI]$_4$ with L = pyridine and morpholine [4]. Copper and iodide atoms together form a cubane core. The present work deals with tetrameric Au(I) complexes. In this case the metal atoms occupy the corners of a square.

2. Experimental

The complexes [Au(dta)]$_4$ [5] (dta = dithioacetate) and [Au(pip)Cl]$_4$ [6] (pip = piperidine) were prepared according to published procedures. Absorption spectra were measured in solution at room temperature on a Uvikon 860 absorption spec-trometer. Emission spectra of the complexes in ethanol glasses at 77 K 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 [Au(dta)]$_4$ in CS$_2$ (fig. 1) displays a band at $\lambda_{max} = 407$ nm ($\epsilon = 1650$)

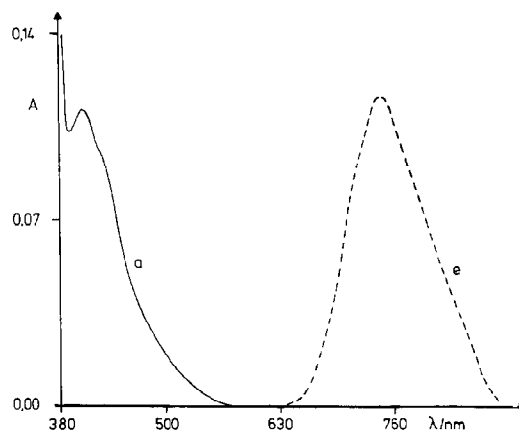Fig. 1. Electronic absorption (a) and emission (e) spectra of [Au(dta)]$_4$. Absorption: 7.29×10^{-5} M in CS$_2$ at room temperature, 1 cm cell. Emission: in C$_2$H$_5$OH at 77 K; $\lambda_{exc} = 430$ nm, intensity in arbitrary units.

which contains a long-wavelength shoulder at 430 nm ($\epsilon = 1400$). These values are close to those reported by Piovesana et al. [5]. The emission of $[Au(dta)]_4$ in ethanol glasses at 77 K was of medium intensity and appears at $\lambda_{max} = 743$ nm (fig. 1). This luminescence was independent of the exciting wavelength ($\lambda_{exc} > 350$ nm) but occurred only at low temperatures. The complex $[Au(pip)Cl]_4$ in ethanol shows its longest-wavelength absorption at $\lambda_{max} = 305$ nm ($\epsilon = 770$). The emission of $[Au(pip)Cl]_4$ in ethanol glasses at 77 K was somewhat weaker than that of the dta complex and appeared at $\lambda_{max} = 700$ nm ($\lambda_{exc} = 250$ nm). Again, there was no luminescence in solutions at room temperature.

4. Discussion

The long-wavelength absorptions of $[Au(dta)]_4$ were tentatively assigned to metal-to-ligand charge transfer (MLCT) transitions [5]. However, based on the similarity of the absorption and emission spectra of $[Au(dta)]_4$ and $[Au(pip)Cl]_4$ we suggest a different assignment since in the latter complex long-wavelength MLCT transitions cannot occur. Neither piperidine nor the chloride ligand provide empty low-energy orbitals.

Both complexes have the same basic structure (I). An important difference is the Au–Au distance, which is smaller in the dta complex (3.013 Å) [5] compared to $[Au(pip)Cl]_4$ (3.301 Å) [6].
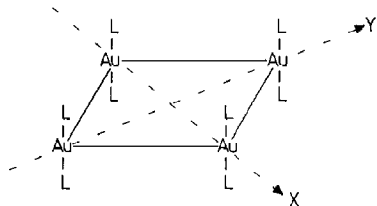
Since for Au(I) the 5d–6s energy separation is rather small and the 5d–6p energy difference very large [7] only appropriate 5d and the 6s orbitals are considered for bonding interactions in the Au_4 cluster. In the Au_4 moiety (D_{4h} symmetry) each Au atom participates with one d and one s orbital in σ interaction with its closest neighbours. The bonding within and the optical lowest-energy transition of the cluster can be explained on the basis of a qualitative MO diagram which is derived from group theoretical
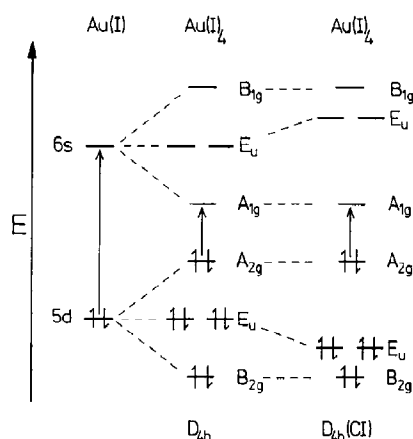

Fig. 2. Qualitative MO diagram of the $Au(I)_4$ moiety including configuration interaction (CI).

considerations (fig. 2) [8]. The metal–metal bonding results only from CI. The d/s mixing leads to stabilization of the occupied degenerate E_u orbitals, which are derived from the 5d atomic orbitals.

For simple mononuclear Au(I) complexes of the type $[AuX_2]^-$ ($X^- =$ halide) the longest-wavelength ds absorptions appear around 40000 cm^{-1} [9]. In the Au_4 cluster the lowest-energy 5d→6s transition $A_{2g} \rightarrow A_{1g}$ (fig. 2) is shifted to lower energies. Consequently, the longest-wavelength bands of $[Au(dta)]_4$ at $\bar{\nu}_{max} = 23255$ cm^{-1} and of $[Au(pip)Cl]_4$ at $\bar{\nu}_{max} = 32786$ cm^{-1} are assigned to the spin-allowed $^1A_{2g} \rightarrow {}^1A_{1g}$ transition. Since it is parity forbidden, these absorptions are only of moderate intensity. Compared to $[Au(pip)Cl]_4$ the Au–Au distance in $[Au(dta)]_4$ is considerably smaller. This may be imposed by the bridging dta ligands [5]. The shorter distance increases the orbital overlap, which decreases the energy gap between HOMO and LUMO. Consequently, the $^1A_{2g} \rightarrow {}^1A_{1g}$ absorption undergoes a red-shift from $[Au(pip)Cl]_4$ to $[Au(dta)]_4$.

The emission of both complexes is assigned to the spin-forbidden $^3A_{1g} \rightarrow {}^1A_{2g}$ transition. While the formal bond order within the Au_4 clusters is zero in the ground state, it is one in the lowest excited state, since an electron is promoted from an antibonding (A_{2g}) to a bonding (A_{1g}) orbital. The large shift from absorption to emission is then at least partially due to the contraction of the Au_4 square which should take

place in the excited state. Compared to $[Au(pip)Cl]_4$ ($\Delta\bar{\nu} = 18500$ cm^{-1}) this shift is much smaller for $[Au(dta)]_4$ ($\Delta\bar{\nu} = 9800$ cm^{-1}). This observation may be explained by the fact that the Au–Au distance in the dta complex is already rather short in the ground state. The excited-state contraction is now expected to be much smaller.

Acknowledgement

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