

ABSORPTION AND EMISSION SPECTRA OF TETRAMERIC GOLD(I) COMPLEXES

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The lowest-energy absorption and emission bands of the complexes $[\text{Au}(\text{dithioacetate})]_4$ and $[\text{Au}(\text{piperidine})\text{Cl}]_4$ 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(I)_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 $[\text{Cu(I)LI}]_4$ with $L = \text{pyridine}$ 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 $[\text{Au}(\text{dta})]_4$ [5] ($\text{dta} = \text{dithioacetate}$) and $[\text{Au}(\text{pip})\text{Cl}]_4$ [6] ($\text{pip} = \text{piperidine}$) 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 $[\text{Au}(\text{dta})]_4$ in CS_2 (fig. 1) displays a band at $\lambda_{\text{max}} = 407 \text{ nm}$ ($\epsilon = 1650$)

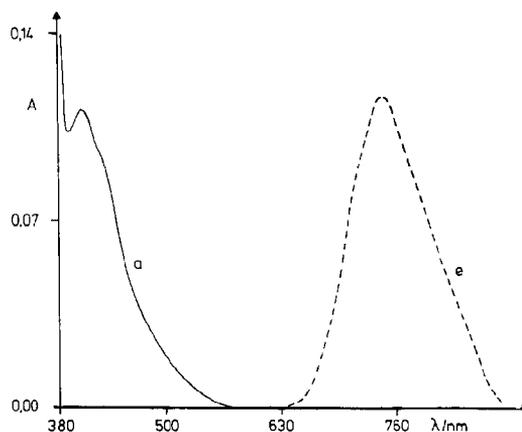


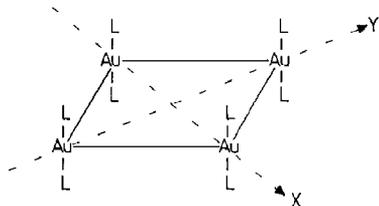
Fig. 1. Electronic absorption (a) and emission (e) spectra of $[\text{Au}(\text{dta})]_4$. Absorption: $7.29 \times 10^{-5} \text{ M}$ in CS_2 at room temperature, 1 cm cell. Emission: in $\text{C}_2\text{H}_5\text{OH}$ at 77 K; $\lambda_{\text{exc}} = 430 \text{ nm}$, intensity in arbitrary units.

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 $[\text{Au}(\text{dta})]_4$ in ethanol glasses at 77 K was of medium intensity and appears at $\lambda_{\text{max}} = 743$ nm (fig. 1). This luminescence was independent of the exciting wavelength ($\lambda_{\text{exc}} > 350$ nm) but occurred only at low temperatures. The complex $[\text{Au}(\text{pip})\text{Cl}]_4$ in ethanol shows its longest-wavelength absorption at $\lambda_{\text{max}} = 305$ nm ($\epsilon = 770$). The emission of $[\text{Au}(\text{pip})\text{Cl}]_4$ in ethanol glasses at 77 K was somewhat weaker than that of the dta complex and appeared at $\lambda_{\text{max}} = 700$ nm ($\lambda_{\text{exc}} = 250$ nm). Again, there was no luminescence in solutions at room temperature.

4. Discussion

The long-wavelength absorptions of $[\text{Au}(\text{dta})]_4$ were tentatively assigned to metal-to-ligand charge transfer (MLCT) transitions [5]. However, based on the similarity of the absorption and emission spectra of $[\text{Au}(\text{dta})]_4$ and $[\text{Au}(\text{pip})\text{Cl}]_4$ 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 $[\text{Au}(\text{pip})\text{Cl}]_4$ (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

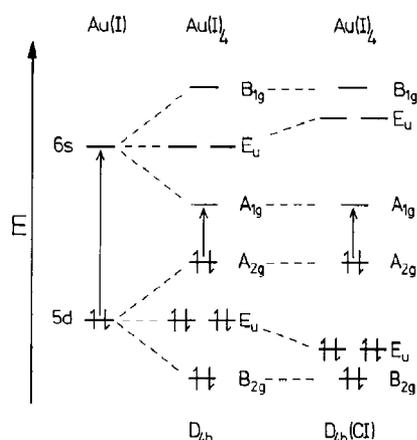


Fig. 2. Qualitative MO diagram of the $\text{Au}(\text{I})_4$ moiety including configuration interaction (CI).

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 $[\text{AuX}_2]^-$ ($X^- = \text{halide}$) the longest-wavelength ds absorptions appear around 40000 cm^{-1} [9]. In the Au_4 cluster the lowest-energy 5d \rightarrow 6s transition $A_{2g} \rightarrow A_{1g}$ (fig. 2) is shifted to lower energies. Consequently, the longest-wavelength bands of $[\text{Au}(\text{dta})]_4$ at $\bar{\nu}_{\text{max}} = 23255 \text{ cm}^{-1}$ and of $[\text{Au}(\text{pip})\text{Cl}]_4$ at $\bar{\nu}_{\text{max}} = 32786 \text{ cm}^{-1}$ 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 $[\text{Au}(\text{pip})\text{Cl}]_4$ the Au–Au distance in $[\text{Au}(\text{dta})]_4$ 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 $[\text{Au}(\text{pip})\text{Cl}]_4$ to $[\text{Au}(\text{dta})]_4$.

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 $[\text{Au}(\text{pip})\text{Cl}]_4$ ($\Delta\bar{\nu}=18500\text{ cm}^{-1}$) this shift is much smaller for $[\text{Au}(\text{dta})]_4$ ($\Delta\bar{\nu}=9800\text{ cm}^{-1}$). 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.

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