

Luminescence Spectroscopy of Monometallic and Bimetallic Platinum(II) Complexes with Triazolopyrimidine Ligands

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Résumé

Les spectres de luminescence de trois complexes du platine(II) à l'état solide et à basse température sont présentés. Les composés $\text{cis-PtCl}_2(\text{Hmtpo})_2$ et $\text{cis-Pt}(\text{NH}_3)_2(\text{Hmtpo})_2(\text{NO}_3)_2$ montrent des bandes larges avec maxima à 16470 cm^{-1} et à 18000 cm^{-1} . Les composés $\text{cis-Pt}(\text{NH}_3)_2(\text{Hmtpo})_2(\text{NO}_3)_2$ et Pt_2mtpo_4 montrent de la structure vibronique résolue avec des intervalles d'approximativement 1500 cm^{-1} . La nature des états initiaux de la luminescence est attribuée à partir des spectres de luminescence, des durées de vie de luminescence et de fréquences vibrationnelles obtenues par spectroscopie Raman. Des transitions d-d ainsi que des transitions d'un état initial centré sur les ligands sont observées.

Abstract

Low-temperature solid-state luminescence spectra of three platinum(II) complexes are presented and discussed. The compounds are $\text{cis-PtCl}_2(\text{Hmtpo})_2$, $\text{cis-Pt}(\text{NH}_3)_2(\text{Hmtpo})_2(\text{NO}_3)_2$, and $\text{Pt}_2(\text{mtpo})_4$, where *Hmtpo* denotes 4,7-H-5-methyl-7-oxo[1,2,4]triazolo[1,5a]pyrimidine. Broad luminescence bands with maxima at 16470 cm^{-1} and 18000 cm^{-1} are observed for the first two compounds, indicating that the lowest-energy electronic transition has significant d-d character. In addition, resolved vibronic structure with bands separated by approximately 1500 cm^{-1} is observed for the last two compounds, indicating that the lowest energy excited state is centered on the triazolopyrimidine ligands. Emitting state assignments are further supported by

luminescence lifetime measurements and Raman spectra.

Keywords: Solid-state spectroscopy, luminescence spectra, platinum(II) complexes, bimetallic complexes

Introduction

Square planar platinum(II) complexes show a rich variety of luminescence properties. Both the square-planar chromophores as well as face-to-face assemblies have received considerable interest (1,2). In the former compounds, it is the vibronic structure of the luminescence spectra and the nature of the emitting state that have been analyzed in detail; in the latter systems, metal-metal bonding and its spectroscopic and photochemical applications have been studied. Some square-planar complexes with nitrogen donor ligands show tunable emitting states (3,4) and bright luminescence in solution even at room temperature (5), an exceptional behavior for transition metal compounds.

We present new low-temperature, single-crystal luminescence spectra of three platinum(II) complexes with triazolopyrimidine ligands. The ligand used is 4,7-H-5-methyl-7-oxo[1,2,4]triazolo[1,5a]pyrimidine, abbreviated as *Hmtpo*, following the recent literature (6,7). The first two compounds, $\text{cis-PtCl}_2(\text{Hmtpo})_2$ and $\text{cis-Pt}(\text{NH}_3)_2(\text{Hmtpo})_2(\text{NO}_3)_2$, crystallize with significant separations between the individual square-planar complexes (6-8). The third complex, Pt_2mtpo_4 , is a bimetallic platinum(II) complex with four *mtpo* bridging ligands that lead to a short metal-metal distance of 2.743 \AA (6). The luminescence behavior illustrates the influence of the different ancillary ligands on luminescence energies, bandshapes and the nature of the emitting state for the first two compounds and the effect of metal-metal interactions for the bimetallic complex. Properties of the

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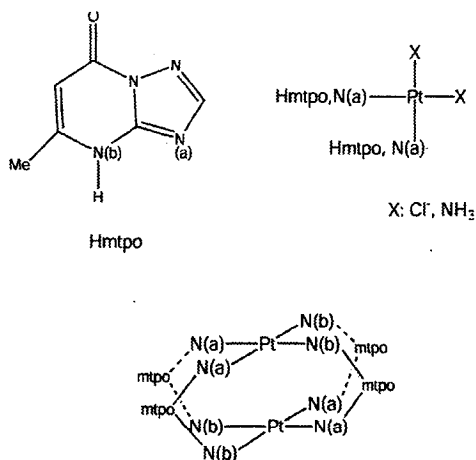


Figure 1. Schematic structures of the Hmtpo ligand, top left, the *cis*-PtCl₂Hmtpo₂ and *cis*-Pt(NH₃)₂Hmtpo₂²⁺ complexes, top right, and the bimetallic Pt₂mtpo₄ complex, bottom. The ligand atoms of the Hmtpo ligand are identified as N(a) and N(b). The mtpo ligands in the bimetallic complex are deprotonated at N(b). The metal-metal distance in Pt₂mtpo₄ is 2.743 Å. The crystalline *cis*-PtCl₂Hmtpo₂ and *cis*-Pt(NH₃)₂Hmtpo₂²⁺ complexes are not stacked and no metal-metal interactions are expected.

ground and emitting states are discussed based on the luminescence spectra, luminescence lifetimes and Raman frequencies presented in the following. The structures of the Hmtpo ligand and all platinum(II) complexes studied in the following are shown schematically in Figure 1.

Experimental

All compounds were prepared using published procedures (6-8) and recrystallized several times before spectroscopic measurements. Crystallographic structures for all compounds have been published (6-8) and the metal-ligand coordination is as given in Figure 1, where the ligand atoms on the Hmtpo ligand are identified. The infrared spectra of samples used for this study are identical to those reported previously (6-8). Luminescence spectra were measured with a Xe lamp as excitation source and a single monochromator (Spex 1800-II) with a photomultiplier and photon counting detection (9). Lifetimes were measured with a pulsed Nd:YAG laser and averaged on a digital oscilloscope (10). The sample temperature was controlled with a He gas flow cryostat (Oxford Instruments CF-1204). Solid-state Raman spectra were measured with a Renishaw System 3000 micro-Raman spectrometer (11,12) using the 488.0 nm and 514.5 nm Ar⁺ ion laser lines as excitation sources.

The lower limit of the frequency range of this instrument is 100 cm⁻¹. Absorption spectra were measured with a Varian Cary 5E spectrometer. All band maxima determined from the spectra were obtained by fitting a Gaussian function to the region near the experimental band maximum.

Spectroscopic Results

The single-crystal luminescence spectra of the title compounds are shown in Figures 2 to 4 as a function of temperature on an identical wavenumber scale for all spectra. These spectra show a remarkable variation of both the energy of the luminescence maximum and the shape of the luminescence band for the series of three complexes schematically shown in Figure 1.

Figure 2 shows the spectra of *cis*-PtCl₂Hmtpo₂. An intense, broad band is observed at low temperatures; its intensity drops by a factor of 3 between 10 K and 77 K. Its maximum is at 16470 cm⁻¹, and its width at half height is 2200 cm⁻¹ at 5 K. Such large, unresolved bands are typical for d-d emissions from square-planar complexes of platinum(II), such as PtCl₄²⁻ with a band maximum at 13000 cm⁻¹ and a width of 2000 cm⁻¹ (2,13). An unresolved luminescence band similar to Figure 2 was reported for *cis*-PtCl₂(bpy) (4,14) and assigned to a crystal field transition for this complex with a ligand sphere very similar to *cis*-PtCl₂Hmtpo₂. Its band maximum and full width at half height are 15600 cm⁻¹ and 4000 cm⁻¹,

Table 1. Luminescence lifetimes and selected vibrational frequencies of the title compounds.

Quantity	<i>cis</i> -PtCl ₂ Hmtpo ₂	<i>cis</i> -Pt(NH ₃) ₂ Hmtpo ₂ (NO ₃) ₂	Pt ₂ mtpo ₄
Luminescence lifetime			
τ [μs] 5 K	55.9	12.3	3.5
τ [μs] 77 K	36.9	6.6	2.1
τ [μs] 150 K	8.9	3.9	1.4
Low-frequency vibrational energies (Raman) [cm ⁻¹]	145, 226, 285, 348, 477, 536	187, 227, 295, 310, 350, 484	107, 117, 230, 249, 265, 298, 501
Ligand-centered vibrational frequencies, from luminescence spectra [cm ⁻¹]	n/a	1333, 1495	1158
Raman frequencies [cm ⁻¹]	1167, 1252, 1317, 1379, 1403, 1588	1048, 1257, 1314, 1343, 1392, 1517	1166, 1256, 1313, 1385, 1534

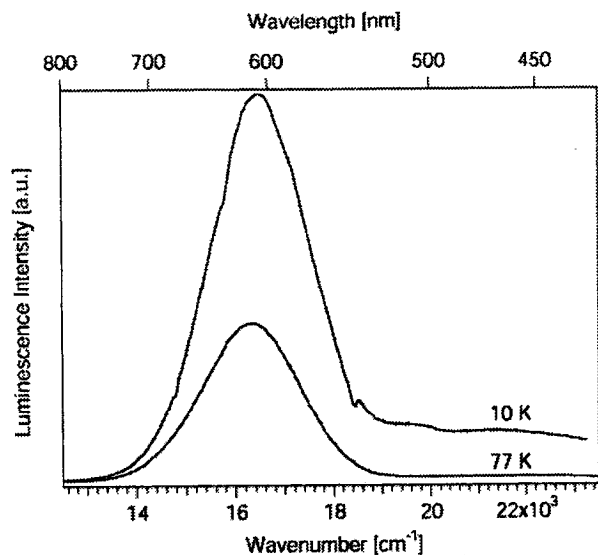


Figure 2. Single-crystal luminescence spectra of *cis*-PtCl₂Hmtpo₂ at 10 K and 77 K.

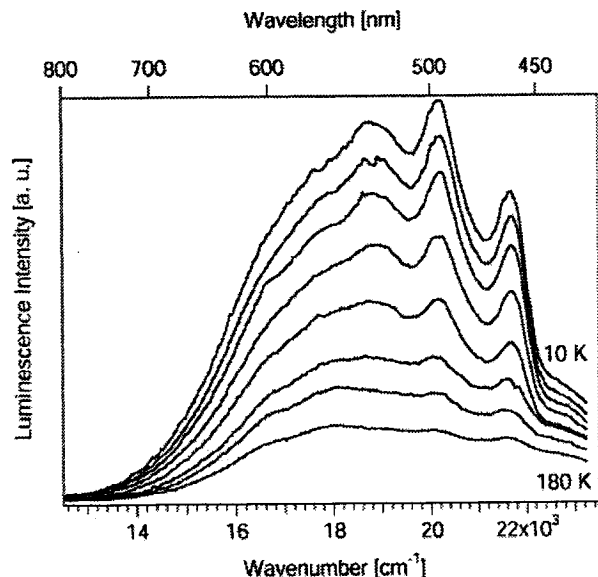


Figure 3. Single-crystal luminescence spectra of *cis*-Pt(NH₃)₂Hmtpo₂(NO₃)₂ as a function of temperature. Temperatures shown (top to bottom): 10 K, 30 K, 50 K, 80 K, 110 K, 130 K, 150 K, 180 K.

respectively, values that corroborate the d-d assignment of the luminescence transition in *cis*-PtCl₂Hmtpo₂.

Figure 3 shows the luminescence spectra of *cis*-Pt(NH₃)₂Hmtpo₂(NO₃)₂. The spectra are shifted to higher energy than the bands shown in Figure 2. A broad band with a maximum at approximately 18000 cm⁻¹, higher in energy by 1500 cm⁻¹ than the maximum in Figure 2 and without clearly resolved structure, is observed at the low-energy side of the spectrum. The

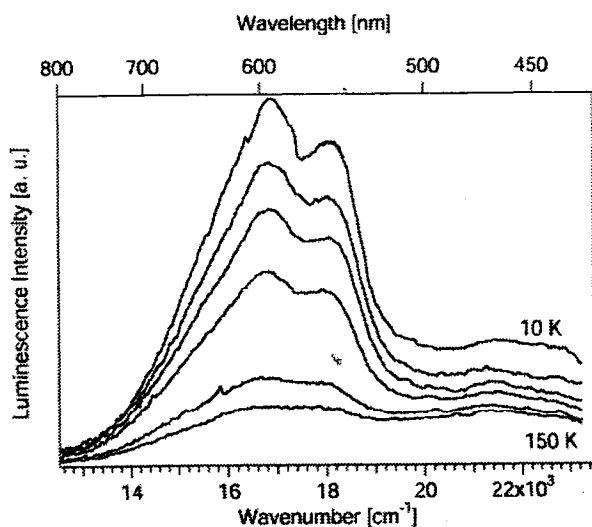


Figure 4. Single crystal luminescence spectra of Pt₂mtpo₄ as a function of temperature. Temperatures shown (top to bottom): 10 K, 30 K, 50 K, 80 K, 130 K, 150 K.

most important change in comparison to Figure 2 occurs at the high-energy side of the spectrum: a series of three peaks are resolved with maxima at 18828 cm⁻¹, 20161 cm⁻¹ and 21656 cm⁻¹. Such resolved peaks with separations larger than 1000 cm⁻¹ are not typical for d-d transitions. Table 1 shows that these intervals correspond to Raman peaks that can be attributed to the Hmtpo ligand. Its most intense Raman maxima in this region are at 1141 cm⁻¹, 1257 cm⁻¹, 1343 cm⁻¹ and 1394 cm⁻¹, values very close to the corresponding Raman frequencies for this complex, as summarized in Table 1. It is therefore likely that the luminescence spectra in Figure 3 have a significant ligand contribution. The intensity ratio of the resolved peaks and the broad band does not change with temperature within experimental accuracy. The overall luminescence intensity decreases by more than an order of magnitude between 10 K and 180 K.

Figure 4 shows the luminescence spectra of the bimetallic complex Pt₂mtpo₄. The luminescence is lower in energy than for the square-planar luminophores in Figure 3. Again, resolved structure is observed with two distinct maxima at 16893 cm⁻¹ and 18051 cm⁻¹, lower in energy by approximately 2000 cm⁻¹ than the resolved maxima in Figure 3. Any unresolved broad bands are hidden below these resolved peaks, whose energy difference again corresponds well to Raman frequencies, as shown in Table 1. The luminescence intensity decreases by more than an order of magnitude between 10 K and 180 K. No luminescence could be observed

from another recently described heterobimetallic complex, $\text{Pt}(\text{NH}_3)_2(\text{m-mtpo})_2\text{Pd}(\text{bpy})(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (7). The emitting state for this complex is expected to be at significantly lower energy than for Pt_2mtpo_4 due to the palladium(II) center (15,16). Intramolecular nonradiative relaxation processes compete very efficiently with such low-energy emissions (17). Intermolecular energy transfer processes to deep traps are another important mechanism leading to quenching of the luminescence. Only very few emission spectra extending to wavelengths beyond 900 nm have been reported for bi- and polymetallic compounds of platinum(II) and palladium(II) (18).

The series of luminescence spectra in Figures 2 to 4 show a distinct variation from unresolved broad bands to spectra with resolved vibronic transitions, covering the large wavenumber range illustrated in the figures. All luminescence intensities decrease with increasing temperature. A corresponding decrease is also observed for the luminescence lifetimes measured near the band maxima and summarized for three temperatures in Table 1. The measured lifetimes are wavelength independent within the precision of our instrumentation. The unresolved, broad band in Figure 2 has the longest lifetime, the higher-energy band system in Figure 3 has a lifetime shorter by a factor of 4 at 5 K, and the luminescence lifetime of the bimetallic compound in Figure 4 is again shorter by a factor of 6 at 5 K. This qualitative correlation indicates that a shorter luminescence lifetime is observed for spectra where the resolved bands become more prominent.

Absorption spectra do not reveal well-defined bands corresponding to the luminescence transitions. Solid samples crystallized onto quartz plates show absorption maxima at approximately 34000 cm^{-1} and 48500 cm^{-1} at 5 K. Room-temperature solution spectra in methanol show a band maximum for all complexes and for the uncoordinated Hmtpo ligand at 34000 cm^{-1} with a molar absorptivity of $330\text{ M}^{-1}\text{cm}^{-1}$ per mole of Hmtpo. This band corresponds, therefore, to the lowest-energy ligand-centered transition. The onsets to this band occur at 30000 cm^{-1} and at 32500 cm^{-1} for $\text{cis-Pt}(\text{NH}_3)_2\text{Hmtpo}_2^{2+}$ and $\text{cis-PtCl}_2\text{Hmtpo}_2$, respectively. This difference indicates that weak charge-transfer transitions occur at lower energy for $\text{cis-Pt}(\text{NH}_3)_2\text{Hmtpo}_2^{2+}$ than for $\text{cis-PtCl}_2\text{Hmtpo}_2$, for which the onset of the band is very similar to that of the uncoordinated ligand. Much lower molar absorptivities of less than $50\text{ M}^{-1}\text{cm}^{-1}$ are observed for $\text{cis-Pt}(\text{NH}_3)_2\text{Hmtpo}_2^{2+}$ and $\text{cis-PtCl}_2\text{Hmtpo}_2$

throughout the visible wavelength range.

Raman transitions for all compounds are summarized in Table 1. We give the low-frequency bands in a range not accessible to routine infrared spectrometers and the ligand-centered bands in the energy range of the resolved luminescence transitions in Figures 2 to 4. A detailed assignment of the low-frequency modes is not possible from the spectra. It is tempting to assign the lowest frequency band of the $\text{Pt}_2(\text{mtpo})_4$ compound at 107 cm^{-1} to a metal-metal mode, especially since it is not observed for the other compounds. This frequency is of the expected magnitude based on literature correlations between Pt-Pt distances, 2.743 \AA in this compound (6), vibrational frequencies and force constants (19), but the assignment is not unambiguous as the band occurs at the low-energy limit of the spectrometer and signals at even lower frequencies can not be measured.

Discussion

The variation of the luminescence spectra for the title compounds in Figures 2 to 4 indicates changes in both the character of the electronic ground and emitting states. This discussion attempts to characterize some of these changes from the spectroscopic results.

The spectra of $\text{cis-PtCl}_2\text{Hmtpo}_2$ in Figure 2 show the typical characteristics of a d-d transition (4). A broad, unresolved band is observed even at low temperature. The large band width is caused by pronounced changes in metal-ligand bonding between the ground and emitting states. The vibrational modes whose normal coordinates define these changes have frequencies on the order of 100 cm^{-1} to 500 cm^{-1} , intervals that are often too small to be resolved. In square-planar d^8 complexes, the d-d transitions involve the population of the s-antibonding $d_{x^2-y^2}$ unoccupied orbital, with the z axis chosen perpendicular to the plane of the complex. This leads to significant bond length changes and to a broad luminescence band (20,21). In square-planar halide complexes, these bond length changes were characterized from resolved single-crystal luminescence spectra (2,15) and from DFT calculations (22). The d-d assignment is further confirmed by the long luminescence lifetime of 55.9 ms at 5 K, a typical value for the lowest-energy crystal field transition which is forbidden by both spin and parity selection rules.

The luminescence spectra of $\text{cis-Pt}(\text{NH}_3)_2\text{Hmtpo}_2(\text{NO}_3)_2$ in Figure 3 consist of two

different regions: a broad, unresolved band dominates between 14000 cm^{-1} and 19000 cm^{-1} and resolved vibronic transitions are observed between 19000 cm^{-1} and 23000 cm^{-1} . We discuss first the broad band, then the resolved vibronic structure. The maximum of the broad band is higher in energy by approximately 1500 cm^{-1} than the band maximum of *cis*-PtCl₂Hmtpo₂ in Figure 2, providing additional experimental evidence for the d-d character of this band. The HOMO-LUMO gap is expected to be larger for *cis*-Pt(NH₃)₂Hmtpo₂²⁺ because the σ -antibonding d_{x²-y²} LUMO is at higher energy due to the ancillary ammonia ligands with nitrogen donor atoms, and the π -antibonding HOMO orbital (d_{xz,yz} or d_{xy}) is lower in energy than for the chloro complex because of absent or weak Pt-NH₃ π -bonding expected for *cis*-Pt(NH₃)₂Hmtpo₂²⁺. The shift of the band maxima is of comparable magnitude to the 3000 cm^{-1} energy difference between the luminescence maximum of PtCl₄²⁻ (2,13) and *cis*-PtCl₂Hmtpo₂, another comparison where two chloro ligands are replaced by nitrogen donors.

We use EHMO calculations to qualitatively analyze the resolved vibronic structure of the luminescence spectra of *cis*-Pt(NH₃)₂Hmtpo₂²⁺ (Figure 3) and to compare with the spectra of Pt₂mtpo₄ (Figure 4). The EHMO calculations (23) were carried out using the crystallographic coordinates from the literature to define the molecular structures (6,7). It is important to note that all calculated energies are obtained for a frozen molecular geometry corresponding to the ground-state structure. The HOMO orbital for the *cis*-Pt(NH₃)₂Hmtpo₂²⁺ complex has predominant d_{xy} character. The LUMO orbital, calculated at an energy higher by 26950 cm^{-1} , is a π^* orbital centered on one of the Hmtpo ligands, with the LUMO+1 orbital centered on the other ligand higher in energy by 920 cm^{-1} . This change of electron density distribution between the HOMO and LUMO, LUMO+1 orbitals leads to the bonding changes on the ligand and to the resolved vibronic transitions in the luminescence spectra in Figure 3. We therefore assign this part of the spectrum as a MLCT band, supported by the good agreement of the resolved energy intervals with Raman frequencies of the uncoordinated Hmtpo ligand. The LUMO+2 orbital has predominant d_{x²-y²} character and is calculated at an energy higher by 4200 cm^{-1} than LUMO+1. The relaxed excited states will have significantly lower energies, and the spectra in Figure 3 indicate that the d-d and MLCT transitions occur at similar energies. Ligand-centered π - π^* luminescence transitions

are expected higher in energy (4) and are therefore ruled out for the spectra in Figure 3. These spectra appear to correspond to a borderline situation; a broad band without resolution is still observed, indicating d-d luminescence, but the resolved peaks of the ligand-centered band are prominent. The temperature dependence of this spectrum does not show a shift from one type of band to the other; their intensity ratio remains constant. This is most likely evidence for emission from two different classes of molecules in these crystals. Even in the presence of energy transfer processes, emission from different luminophores has been observed (9). The more highly allowed charge-transfer transition leads to a shorter luminescence lifetime than measured for *cis*-PtCl₂Hmtpo₂, and energy transfer processes likely prevent the measurement of the longer lifetime for the d-d transition leading to the broad band in Figure 3. The measurement of individual lifetimes for this compound is difficult due to the large overlap of the broad and structured regions of the luminescence spectra. For luminescence from a single type of molecule with two emitting states in thermal equilibrium, a change of the intensity ratio with temperature is expected (24). Nevertheless, the observation of two types of luminescence bands indicates that the ligand- and metal-centered emitting states are close in energy, in contrast to *cis*-PtCl₂Hmtpo₂, where the weak chloro ligands lower the crystal-field emitting state below all ligand-centered states.

The spectra for Pt₂mtpo₄ show predominant intensity from the vibronic bands assigned as ligand-centered vibrational modes in the preceding section. This indicates that the emitting state is ligand-centered, in analogy to the assignment for *cis*-Pt(NH₃)₂Hmtpo₂²⁺. The resolved maxima in Figure 4 are shifted to lower energy by approximately 2000 cm^{-1} compared to the corresponding transitions in Figure 3. EHMO calculations confirm that this energy difference is due to a change of the molecular electronic structure in the ground state. The HOMO orbital is σ -antibonding and consists mainly of the d_{z²} orbitals of the two platinum(II) centers. The metal-metal interaction destabilizes the calculated HOMO by approximately 6000 cm^{-1} compared to *cis*-Pt(NH₃)₂Hmtpo₂²⁺ and the HOMO-LUMO difference decreases to 20900 cm^{-1} , lower by more than 20% than for *cis*-Pt(NH₃)₂Hmtpo₂²⁺. This effect is likely the origin of the shift to lower energy observed for the resolved peaks in Figure 4 compared to Figure 3. Even though no

clear assignment of a metal-metal mode could be made from the Raman spectrum, it is very likely that the short metal-metal distance has a significant effect on the luminescence energy. Luminescence spectroscopy therefore proves to be a good complementary tool for the characterization of metal-metal interactions, in particular when related compounds are compared.

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