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Pressure-induced variations of MLCT and ligand-centered luminescence spectra in square-planar platinum(II) complexes

Alexandre Rodrigue-Witchel [a], David L. Rochester [b], Shu-Bin Zhao [c], Kevin B. Lavelle [d], J.A. Gareth Williams [b], Suning Wang [c], William B. Connick [d], Christian Reber [a,*]

[a] *Département de Chimie, Université de Montréal, Montréal, Québec H3C 3J7, Canada*
[b] *Department of Chemistry, Durham University, Durham DH1 3LE, UK*
[c] *Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada*
[d] *Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, OH 45221-0172, United States*

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ABSTRACT

Solid-state luminescence spectra of five crystalline platinum(II) complexes at variable pressure and temperature are presented and compared. Maxima occur between 14 000 cm^{-1} and 15 600 cm^{-1} (approximately 700–640 nm) at ambient temperature and pressure. Spectra can be broad bands, characteristic of MLCT transitions, or vibronically structured, characteristic of intraligand transitions. Both pressure and temperature variations can lead to distinctive changes in the luminescence spectra that differ between these two types of transitions. MLCT band maxima show shifts on the order of $-20\ cm^{-1}$/kbar to lower energy; in contrast, ligand-centered luminescence bands do not show significant shifts between ambient pressure and 40 kbar.

1. Introduction

Square-planar complexes with the d^8 electron configuration are attractive building blocks for a variety of luminescent materials, due to their unsaturated coordination sphere [1]. Such compounds are studied as emitters for OLEDs [2] and for bioimaging [3], as they often show intense luminescence at room temperature [1,3]. Aggregation is a key consideration because of its effects on luminescence energies and intensities [4]. Chemical variations can be used to modify the effects of aggregation [5]. Variations of ligands can lead to changes of both the molecular electronic structure [6] and the packing, making it challenging to explore individual contributing factors. Changes of the environment only, e.g. from crystals to solutions, or vapochromic effects, offer a more continuous variation. In this paper, we present results based on a continuous variation of the environment through external pressure leading to significant and characteristic effects on the luminescence spectra [7].

Pressure-induced trends reveal particularly rich information, with shifts of luminescence maxima that can vary between $-400\ cm^{-1}$/kbar [8] and $+50\ cm^{-1}$/kbar, a range wide enough to allow a classification of transitions and properties. Shifts for d–d luminescence maxima are well documented and range from approximately $+10\ cm^{-1}$/kbar to $+50\ cm^{-1}$/kbar [9,10]. Shifts to lower energy, between $-100\ cm^{-1}$/kbar and $-400\ cm^{-1}$/kbar, occur for compounds with strong metal–metal interactions such as tetracyanoplatinates [8,11]. The results presented here fill the gap in these ranges and document the behavior of MLCT and ligand-centered transitions.

The schematic structures and abbreviations for the five platinum(II) complexes used in this study are shown in Scheme 1. The complexes are neutral and have different ligands with extended π systems, influencing stacking in the crystals and excited-state energies.

2. Experimental

The syntheses and characterization of all compounds have been published [5,6,12–14]. Luminescence and Raman spectra were measured using an InVia spectrometer coupled to an imaging microscope (Leica) and argon ion lasers. The excitation wavelength used was 488 nm for all luminescence measurements and 785 nm for the Raman spectra. Variable-temperature spectra were measured using a Linkam gas-flow microcryostat system and variable-pressure spectra with a diamond anvil cell (High Pressure Diamond Optics, Inc.). Pressure was determined by monitoring the luminescence of a ruby chip included with the sample in the diamond anvil cell [7,9]. Ruby luminescence is denoted by asterisks in Figs. 1–3.

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* Corresponding author. Tel.: +1 514 343 7332; fax: +1 514 343 7586.
E-mail address: christian.reber@umontreal.ca (C. Reber).

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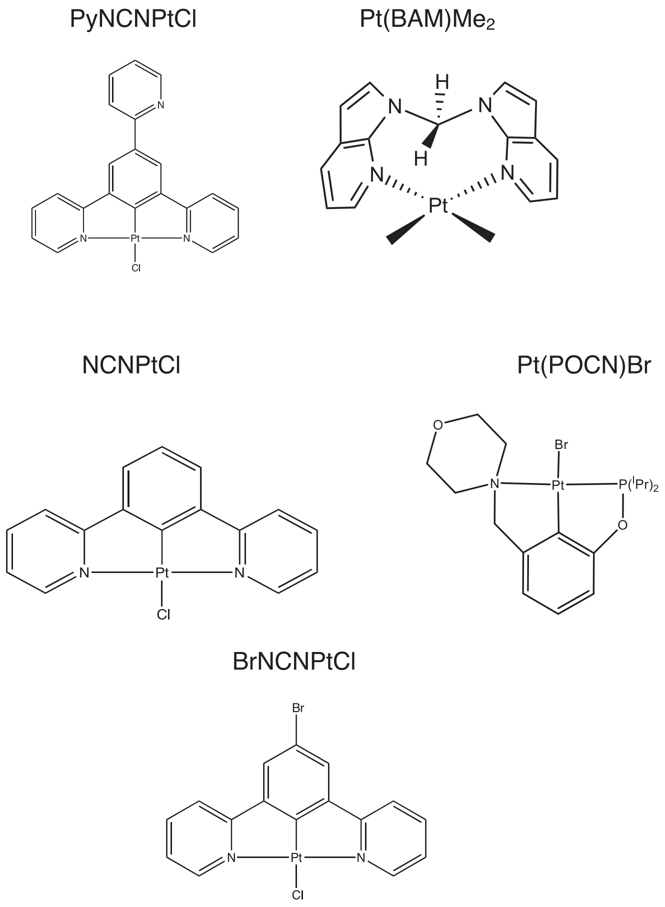

Scheme 1. Schematic structures and abbreviations used for the title compounds. Top to bottom: PyNCNPtCl:1,3,5-tri(2-pyridyl)benzene platinum(II) chloride; Pt(BAM)Me$_2$: bis(7-azaindol-1-yl)methanePt(CH$_3$)$_2$; NCNPtCl: 1,3-di(2-pyridyl)benzene platinum(II) chloride; Pt(POCN)Br: κ^P, κ^C, κ^N-[2,6-(iPr$_2$PO)-(C$_6$H$_3$)(CH$_2$[c-N(CH$_2$)$_4$O])]PtBr; BrNCNPtCl: 1-bromo-3,5-di(2 pyridyl)benzene platinum(II) chloride.

2.1. Spectroscopic results

Luminescence spectra of the five crystalline platinum(II) complexes are shown in Figs. 1–5 at variable temperature and pressure. Values of the pressure-induced shifts are given in Table 1. BrNCNPtCl in Fig. 1 shows a single broad band at all temperatures and pressures explored. The band maximum shifts to lower energy with increasing pressure and decreasing temperature, as shown in Fig. 1. Trends of band maxima in the same direction at high pressure and low temperature are expected, as both variations lead to a decrease of the sample volume [10]. The maximum shifts by +2.6 cm^{-1}/K. The band width increases from 1100 cm^{-1} to 1500 cm^{-1} between 80 K and room temperature, the characteristic signature of a vibronic intensity mechanism, as intensity increases mainly to the high-energy side of the electronic origin. This effect contributes to the shift of the maximum to higher energy as temperature increases [15].

The luminescence spectra of PyNCNPtCl at variable pressure are presented in Fig. 2 and show a behavior similar to BrNCNPtCl in Fig. 1. A broad band with its maximum at approximately 14000 cm^{-1} again shifts to lower energy as pressure increases. Spectra recorded at variable temperature show two luminescence features at temperatures below 150 K: a broad band similar to Fig. 1b with its maximum at approximately 14000 cm^{-1}, and a more highly structured band at approximately 18000 cm^{-1}. At room temperature, this second band disappears.

The NCNPtCl complex shows a broad band without resolved structure at pressures higher than 10 kbar, illustrated in Fig. 3a. At ambient pressure and variable temperature, the spectrum in Fig. 3b shows some resolved structure, indicating a transition of a different nature than for the previous two complexes.

Fig. 4 shows luminescence spectra of the platinum(II) pincer complex Pt(POCN)Br [13]. A broad band with a maximum at approximately 15000 cm^{-1} is observed at room temperature and ambient pressure. The variable-pressure spectra in Fig. 4a show very little variation as pressure increases. The luminescence intensity increases at low temperature, as shown in Fig. 4b.

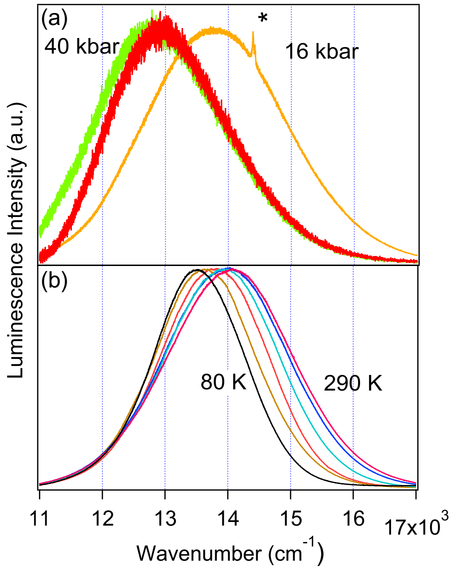

Fig. 1. Luminescence spectra of BrNCNPtCl at variable pressure (16 kbar, 28 kbar and 40 kbar) (a) and at variable temperature (80, 130, 180, 230, 270 and 290 K) (b). The peaks denoted by * are ruby luminescence used for pressure calibration.

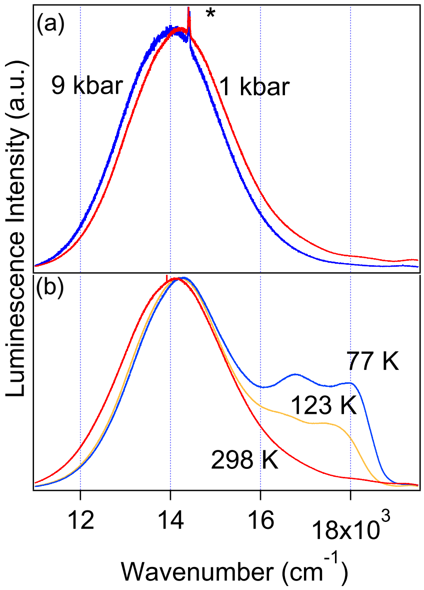

Fig. 2. Luminescence spectra of PyNCNPtCl at variable pressure (a) and at variable temperature (b). The peaks denoted by * are ruby luminescence used for pressure calibration.