Electronic Supplementary Information

Large d-d luminescence energy variations in square-planar bis(dithiocarbamate) platinum(II) and palladium(II) complexes with near-identical MS₄ motifs: a variablepressure study

Stéphanie Poirier, Feriel Rahmani, Christian Reber

Département de chimie, Université de Montréal, Montréal, Québec, H3C 3J7, Canada

Electronic Supplementary Information (ESI) available: Table of luminescence band maxima E_{max} for square-planar platinum(II) and palladium(II) complexes (literature), variable-pressure luminescence spectra, variable-pressure FWHM, variable-pressure and variable-temperature Raman spectra, cif file of [Pt(bmpDTC)₂] at 150 and 295 K (CCDC: 1527919-1527920).

Table of Contents

Table S1: Comparison of ambient pressure luminescence band maxima (E_{max}) for square-planar platinum(II) and palladium(II) complexes
Figure S1. Luminescence specta at variable pressure of crystals of [Pt(bmpDTC) ₂] from 0 kbar (red) to 44 kbar (purple). Intensities were measured as shown
Figure S2. FWHM at variable pressure for [Pt(bmpDTC) ₂] (blue) and [Pd(bmpDTC) ₂] (red). FWHM at variable pressure is not shown above 30 kbar for [Pt(bmpDTC) ₂], as the noise level contributes too significantly in the measure of the width
Figure S3. Raman spectra at variable pressure for $[Pt(bmpDTC)_2]$. The inset shows a zoom of the 200-500 cm ⁻¹ region to illustrate the shifts of peaks towards higher frequency and broadening with pressure
Figure S4. Raman spectra at variable pressure for $[Pd(bmpDTC)_2]$. The inset shows a zoom of the 200- 500 cm ⁻¹ region to illustrate the shifts of peaks towards higher frequency and broadening with pressure 6
Figure S5. Raman spectra at variable temperature for [Pt(bmpDTC) ₂]. The inset shows a zoom of the 200- 500 cm ⁻¹ region to illustrate the absence of variations of the peak pattern with temperature that could indicate a phase transition
Figure S6. Raman spectra at variable temperature for $[Pd(bmpDTC)_2]$. The inset shows a zoom of the 200-500 cm ⁻¹ region to illustrate the absence of variations of the peak pattern with temperature that could indicate a phase transition
Figure S7. Variation of the asymmetric stretching frequency of the C-S bonds as conditions are varied in Raman spectroscopy for [Pd(bmpDTC) ₂] (red) and [Pt(bmpDTC) ₂] (blue)

Compound	$E_{max}(cm^{-1})$	Difference	Difference	T(K)	Ref
		(cm^{-1})	(%)		
$K_2[PtBr_4]$	12500	2150	17	5	1
$K_2[PtCl_4]$	12800			5	1
$K_2[Pt(SCN)_4]$	14650			100	2
[Pt(EDTC) ₂]	16000	3000	23	293	3
[Pt(bmpDTC) ₂]	15600			293	This work
$[Pt{(CH_3)_2DTC}_2]$	14200			293	4, 5
[Pt(dopDTC) ₂]	13000			293	4
$K_2[PdBr_4]$	10900	1500	14	100	6
K ₂ [PdCl ₄]	11100			100	6
$(n-Bu_4N)_2[Pd(SCN)_4]$	12400			70	7
[Pd(EDTC) ₂]	14400	1400	12	293	3
[Pd(PDTC) ₂]	14300			293	3
[Pd(bmpDTC) ₂]	14600			293	This work
$[Pd{(CH_3)_2DTC}_2]$	13000]		293	5, 8

Table S1: Comparison of ambient pressure luminescence band maxima (Emax) for square-plan	ıar
platinum(II) and palladium(II) complexes.	



Figure S1. Luminescence specta at variable pressure of crystals of [Pt(bmpDTC)₂] from 0 kbar (red) to 44 kbar (purple). Intensities were measured as shown.



Figure S2. FWHM at variable pressure for [Pt(bmpDTC)₂] (blue) and [Pd(bmpDTC)₂] (red). FWHM at variable pressure is not shown above 30 kbar for [Pt(bmpDTC)₂], as the noise level contributes too significantly in the measure of the width.



Figure S3. Raman spectra at variable pressure for $[Pt(bmpDTC)_2]$. The inset shows a zoom of the 200-500 cm⁻¹ region to illustrate the shifts of peaks towards higher frequency and broadening with pressure.



Figure S4. Raman spectra at variable pressure for $[Pd(bmpDTC)_2]$. The inset shows a zoom of the 200-500 cm⁻¹ region to illustrate the shifts of peaks towards higher frequency and broadening with pressure.



Figure S5. Raman spectra at variable temperature for $[Pt(bmpDTC)_2]$. The inset shows a zoom of the 200-500 cm⁻¹ region to illustrate the absence of variations of the peak pattern with temperature that could indicate a phase transition.



Figure S6. Raman spectra at variable temperature for $[Pd(bmpDTC)_2]$. The inset shows a zoom of the 200-500 cm⁻¹ region to illustrate the absence of variations of the peak pattern with temperature that could indicate a phase transition.



Figure S7. Variation of the asymmetric stretching frequency of the C-S bonds as conditions are varied in Raman spectroscopy for [Pd(bmpDTC)₂] (red) and [Pt(bmpDTC)₂] (blue).

References:

- 1. H. Yersin, H. Otto, J. I. Zink and G. Gliemann, J. Am. Chem. Soc., 1980, 102, 951-955.
- 2. I. Hidvegi, W. Tuszynski and G. Gliemann, Chem. Phys. Lett., 1981, 77, 517-519.
- 3. C. Genre, G. Levasseur-Thériault and C. Reber, Can. J. Chem., 2009, 87, 1625-1635.
- 4. S. Poirier, R. J. Roberts, D. Le, D. B. Leznoff and C. Reber, *Inorg. Chem.*, 2015, **54**, 3728-3735.
- 5. S. Poirier, P. Guionneau, D. Luneau and C. Reber, Can. J. Chem., 2014, 92, 958-965.
- 6. Y. Pelletier and C. Reber, *Inorg. Chem.*, 1997, **36**, 721-728.
- 7. J. K. Grey, I. S. Butler and C. Reber, J. Am. Chem. Soc., 2002, 124, 9384-9385.
- 8. S. Poirier, E. Tailleur, H. Lynn and C. Reber, *Dalton Trans*, 2016, 45, 10883-10886.