

d-d luminescence energy variations in square-planar complexes with d⁸ metal ions: a variable pressure study

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The comparison of luminescence band maxima E_{\max} of several square-planar complexes of nickel(II), palladium(II) and platinum(II) with dithiocarbamate ligands with different peripheral substituents shows significant variations of the d-d luminescence maxima E_{\max} despite very similar metal coordination geometries. Luminescence spectroscopy at variable pressure reveal the effects of small structural differences and intermolecular $M\cdots H-C$ interactions on the variation of E_{\max} values of several complexes.^[1] $\Delta E_{\max}/\Delta P$ values can be interpreted to understand the strength of intermolecular interactions involving the metal as pressure varies, leading to a variety of effects related to the crystal packing and structure.^[2] Example of negative $\Delta E_{\max}/\Delta P$ values and strongly positive $\Delta E_{\max}/\Delta P$ values are discussed. Structural mobility and initial position of the H atoms involved in the interactions have a significant effect on E_{\max} and $\Delta E_{\max}/\Delta P$, with a stronger impact on platinum(II) complexes than on isostructural palladium(II) analogs. Structures at variable pressure were measured to determine the structural changes.

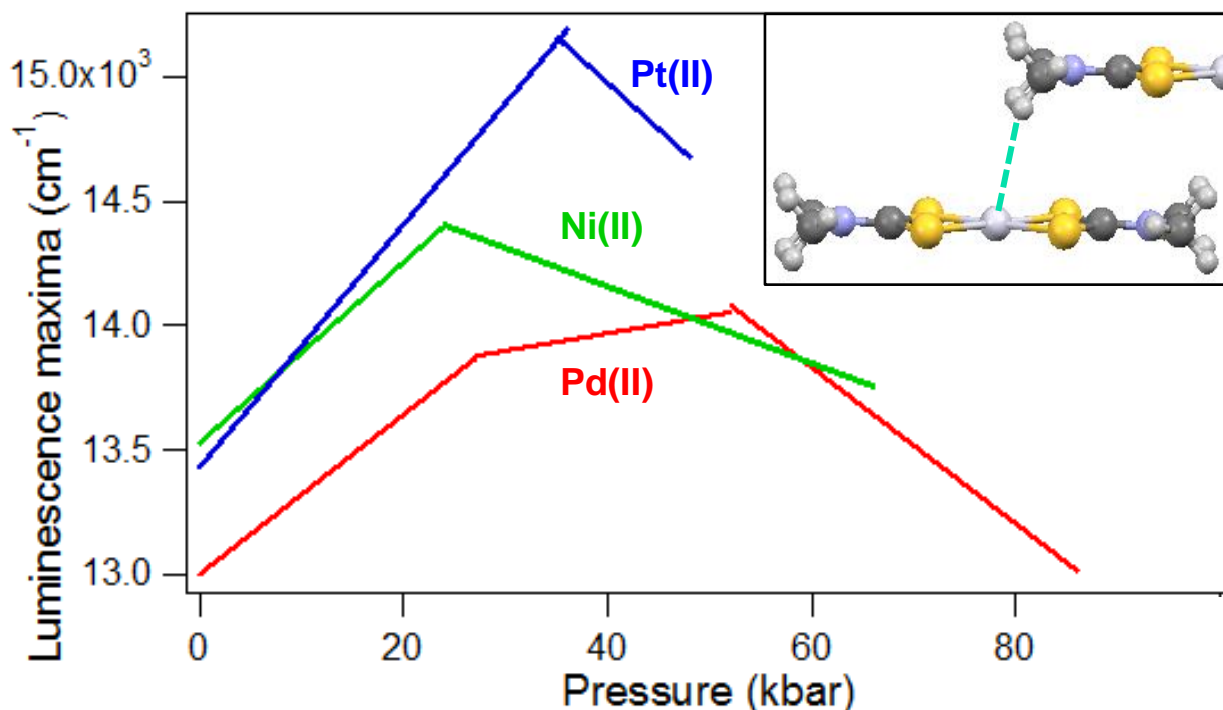


Figure 1. Variation of the luminescence maxima with pressure for dimethyldithiocarbamate complexes with a $M\cdots H-C$ interaction. Pt(II) metal center is in blue, Pd (II) in red and Ni(II) in green.

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References:

- [1] S. Poirier, F. Rahmani, C. Reber, *Dalton Trans. CSC100: Celebrating Canadian Chemistry* **2017**, accepted
- [2] S. Poirier, E. Tailleur, H. Lynn, C. Reber, *Dalton Trans.* **2016**, 45, 10883