

Investigation of the Metal-sulfur Interaction in Pd(ii) and Pt(ii) Complexes of 1,4,7-trithiacyclononane by Pressure-dependent Luminescence Spectroscopy

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Extensive structural studies of Pt(II) and Pd(II) complexes of 1,4,7-trithiacyclononane (9S3), found in the literature, have shown an interesting long range axial interaction between the metal centre and the third sulfur of the 1,4,7-trithiacyclononane ligand. The nature and strength of this interaction is the subject of current debate.



In this project, Pd(9S3)Cl₂ and Pt(9S3)Cl₂ were synthesized according to literature procedures and the novel complexes [Pd(9S3)(en)][PF₆]₂ and [Pt(9S3)(en)][PF₆]₂ were synthesized and fully characterized. Luminescence spectroscopy was used to study these complexes at high pressures in the solid state. In contrast to simple square planar Pd(II) and Pt(II) complexes, the luminescence band maxima of which show a blue shift with pressure of approximately +25 cm⁻¹/kbar, the Pd(II) 1,4,7-trithiacyclononane complexes show a much smaller blue shift, on the order of +5 cm⁻¹/kbar, while the Pt(II) complexes show a red shift on the order of -25 cm⁻¹/kbar. We conclude that two effects are present – a blue shift due to equatorial ligand bond shortening and a red shift due to the approach of the axial sulfur to the metal centre. One effect or the other dominates depending on the metal and the ancillary ligand L.