

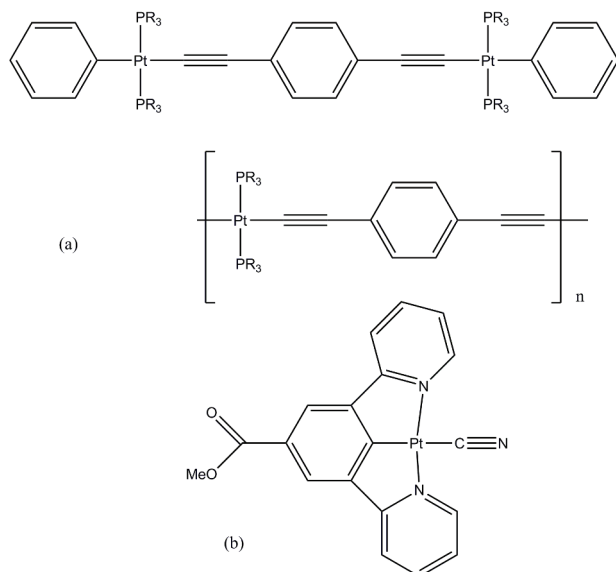
**KN-12** Molecular structure and luminescent propertiesPaul R. Raithby<sup>1</sup>

1. Department of Chemistry, University of Bath, UK

email: p.r.raithby@bath.ac.uk

Luminescence can either take the form of fluorescence, emission of a photon from a singlet excited state, or phosphorescence, emission from an excited triplet state. The fluorescent emission normally occurs on a much faster timescale than phosphorescence. Being able to exploit phosphorescence emission enhances the emission efficiency, since there are three accessible triplet states for each singlet state. However, in order to achieve this singlet to triplet intersystem crossing has to occur. This is facilitated by the presence of heavy transition metals, such as osmium, iridium or platinum, with their associated high spin-orbit coupling. Thus, there has been considerable interest in platinum(II) poly-yne complexes and polymers which display excellent phosphorescence properties. These materials take the form of platinum (II) dimers linked by an aromatic or heteroaromatic linker group, or related polymers (Figure 1a).<sup>1</sup> In these systems we have found it possible to tune the electronic band gap, and the luminescent properties, by changing the donor/acceptor properties of the linker group, its length and the properties of auxiliary ligands on the metal centres.<sup>2</sup> More recently, we have found that related platinum(II) pincer complexes (Figure 1b) show changes in their colour and luminescent properties depending on how they pack in the solid-state. This packing, and hence the luminescence, can be modified by the introduction of various solvents and volatile organic compounds into the crystal. These colour changes occur on a sub-second time scale providing a new class of rapid-acting sensors.

**References** <sup>1</sup> Chawdhury, N.; et. al. *J. Chem. Phys.* **1999**, *110* (10), 4963-4970. <sup>2</sup> Devi, L. S.; et. al. *Macromolecules* **2009**, *42* (4), 1131-1141.



**Figure 1.** Figure 1. The structures of (a) the platinum (II) diynes and poly-ynes, and (b) the structures of some platinum (II) pincer complexes.

**Keywords:** Platinum (II), Diynes, Poly-ynes, Pincer complexes, Luminescence, X-ray crystal structures

**KN-13** Structure determination revisitedGeorge M. Sheldrick<sup>1</sup>

1. Institute of Inorganic Chemistry, Göttingen, Germany

email: gsheldr@shelx.uni-ac.gwdg.de

Recent developments in the experimental phasing of both small and macromolecules with the SHELX programs will be discussed. In both cases the amount of user input required has been reduced to an absolute minimum.

The new program SHELXT (released August 2014) for small molecule structure solution requires only the unit-cell, Laue group, reflection data and an approximate indication of which elements might be present. The phase problem is solved for data expanded to space group P1 and the resulting phases are then used to determine the true space group. This is much more robust than conventional methods based on systematic absences etc. The integrated electron density enables most elements to be identified correctly.

The programs SHELXC, SHELXD and SHELXE apply the SAD, MAD, SIRAS, SIR and RIP methods for experimental phase determination followed by density modification and iterative poly-alanine tracing. SHELXE may also be used to improve borderline molecular replacement solutions. The statically linked SHELX programs have zero dependencies - no libraries, other programs or environment variables are required - and are available free for academic use for Windows, Linux and MacOSX systems. Further details may be found on the SHELX homepage.

**Keywords:** SHELX, Phase problem, Experimental phasing