Multisensors based on palladium metal complexes

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An ideal chemical sensor offers complete selectivity in response to any desired concentration or attribute of the target material or substance, irrespective of the properties of the local environment or of other components present, in order to deliver an unambiguous measurable output. However, real-world chemical sensors are restricted across most or all of these criteria, and are only viable for specific circumstances of measuring medium, concentration and other parameters. The expansion in the range of sensors over recent decades, although impressive, has been consistently outstripped by the need to detect and measure more substances at differing concentrations and in different environments. New types of sensors, possibly working on novel principles, are therefore of considerable interest, with sensors capable of measuring different attributes (multisensors) being particularly attractive candidates for development.

Our interest in multisensors had its origins in high pressure crystallographic studies of palladium macrocyclic complexes, the colour of which showed an unprecedented sensitivity to pressure (see Figure 1 for an example). Further investigations showed that the same complex is also sensitive to the presence of

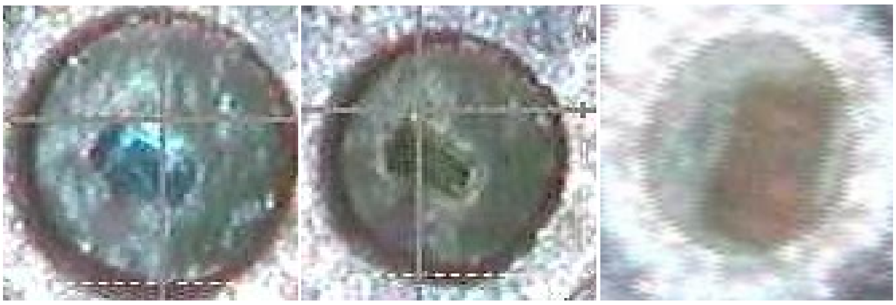

Figure 1. Views of a crystal of a palladium complex at (L–R): 1.2 kbar (blue), 49.3 kbar (green) and 51.0 kbar (orange).

both water and specific volatile organic compounds (VOCs). Perhaps the most intriguing aspect of the piezochromism is the total encapsulation of the Pd(II) chromophore: Why does it respond so strongly to the external environment? The piezochromism may depend on outer-sphere effects, which could lead to a highly robust sensor. We have identified a complex array of intermolecular interactions which could be responsible, but we now need to discover which of these are essential, which are ancillary and which are incidental, and so establish the degree of complexity required for these sensor functions.

The multisensors project has reached a crucial stage where it is poised to expand from the discovery and rationalisation of new phenomena to their application in practical devices. We propose a multidisciplinary advance on three fronts:
(i) Deposition of palladium complexes on optical fibres using established methods [1]; measurement of analyte concentrations by evanescent wave absorption spectroscopy [2]; investigation of the stability of the devices and their sensitivity and selectivity towards VOCs in different media. Locale: Engineering
(ii) Investigations of the mechanisms of piezochromism by experimental (*e.g.*, spectroscopic) and theoretical (*e.g.*, DFT) methods. Locale: Chemistry and Engineering
(iii) Identification and characterisation of further macrocyclic complexes as potential sensor materials for different analytes and media. We are superbly equipped [3] to deploy high pressure techniques to amplify and thereby identify relevant interactions between the components of each complex. Locale: Chemistry

The overall aim is to generate an efficient pipeline of fully characterised complexes for incorporation and evaluation as sensor materials.

References

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